Controlling molecular rotary motion with a self-complexing lock

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Supporting Information

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Controlling Molecular Rotary Motion with a Self-Complexing Lock**

*Da-Hui Qu and Ben L. Feringa**

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General remarks for synthetic procedures:

Reagents were purchased from Aldrich, Acros, Strem, Merck or Fluka and were used as provided unless otherwise stated. All solvents were reagent grade and were dried and distilled prior to use according to standard procedures. All reactions were performed in oven- or flame-dried round bottomed or modified Schlenk (Kjeldahl shape) flasks fitted with rubber septa under a positive pressure of nitrogen, unless otherwise noted. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation 30-40 °C. Flash column chromatography was performed as described by Still et al. (Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2925). Chromatography: silica gel, Merck type 9385 230-400 mesh.

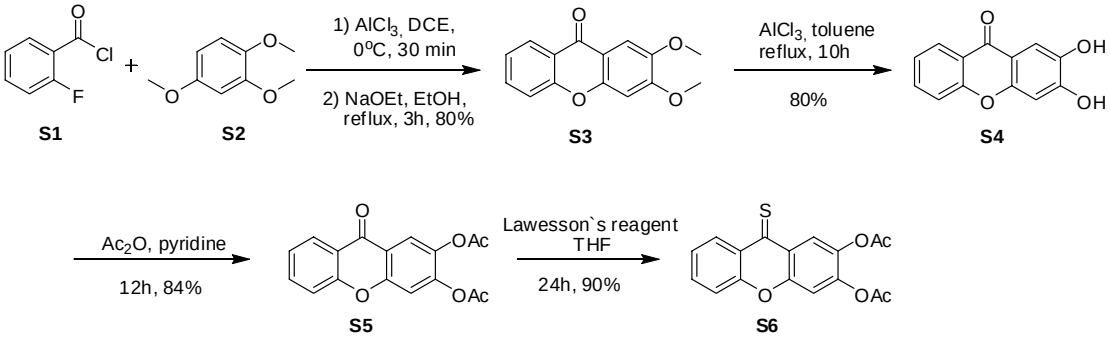
TLC: silica gel 60, Merck, 0.25 mm, impregnated with a fluorescent indicator (254 nm). TLC plates were visualized by exposure to ultraviolet light (UV) and/or exposure to ceric ammonium molybdate solution (CAM) or an acidic solution of p-anisaldehyde (anisaldehyde) followed by brief heating with a heating gun.

Mass spectra (HRMS) were recorded on an AEI MS-902. Melting points were recorded on a Büchi B-545 melting point apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Varian VXR-300, a Varian Mercury Plus, or a Varian Inova 500 operating at 299.97, 399.93 and 499.98 MHz, respectively.

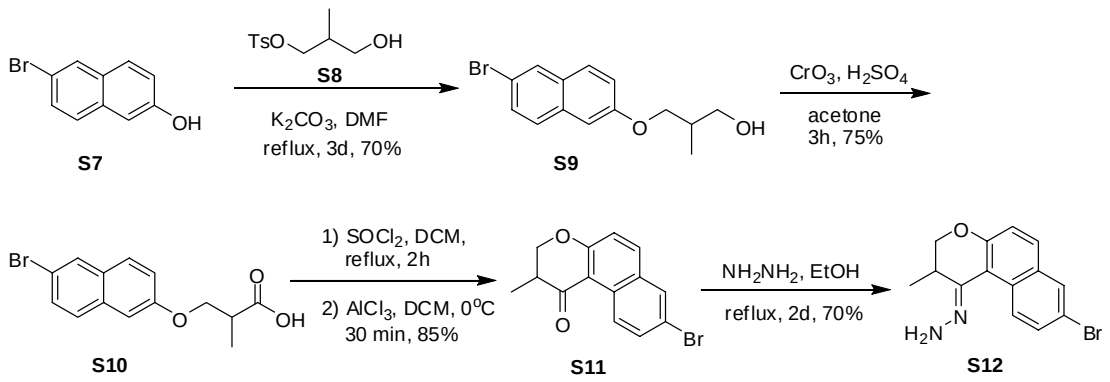
Irradiation experiments were performed using a Spectroline model ENB-280C/FE lamp at λ = 365 nm, ± 30 nm. NMR samples were placed 2-3 cm from the lamp.

UV-vis spectra were obtained using a Hewlet-Packard HP 8543 FT spectrophotometer in a 1 cm quartz cuvette.

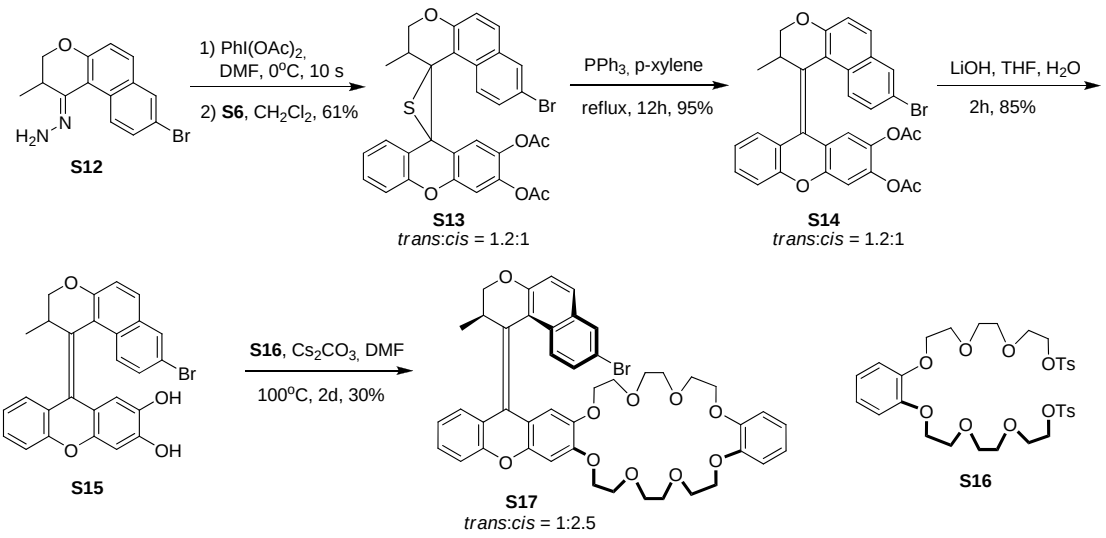
Synthesis of compounds and intermediates



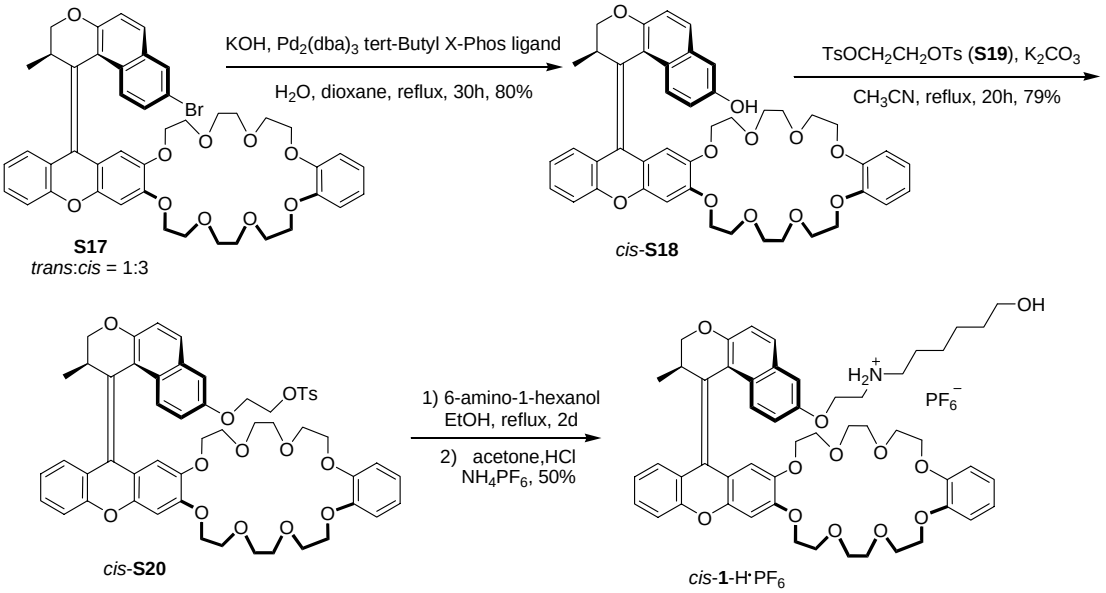
Scheme S1. Synthesis of lower-half thioketone **S6**.



Scheme S2. Synthesis of upper-half hydrazone **S12**.



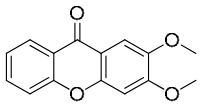
Scheme S3. Synthesis of bromo-substituted crown ether motor **S17**.



Scheme S4. Synthesis of target motor ***cis*-1-H·PF$_6$**.

Compound **S8** [1], **S16** [2] were prepared according to literature procedures.

2,3-dimethoxy-*9H*-xanthen-9-one (S3)

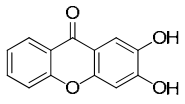


S3

2-Fluorobenzoyl chloride (11.3 g, 71.43 mmol) and 1,2,4-trimethoxybenzene (12 g, 71.35 mmol) were dissolved in 1,2-dichloroethane (100 mL) and cooled to 0 °C. $AlCl_3$ (11 g, 90 mmol) was added to the mixture in 1 h at 0 °C. The mixture was allowed to warm to room temperature, and subsequently heated at reflux for 1 h to give a dark solution. After cooling down to room temperature, 20 mL conc. HCl and 30 mL ice water were carefully added to quench the reaction. The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was washed with brine and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure. The brown residue was then dissolved in ethanol (250 mL) and sodium methoxide (8 g, 0.18 mol) was added. The mixture was heated at reflux for 3 h, and

then half of the solvent was removed under reduced pressure. The precipitate was filtered and washed with water and ethanol to give a white solid (14.6 g, 80 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.01 (s, 3H), 4.03 (s, 3H), 6.94 (s, 1H), 7.39 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.67-7.72 (m, 2H), 7.15 (dd, *J* = 9.2, 2.4 Hz, 1H). ^{13}C NMR (APT, 100 MHz, CDCl3) 56.6 (q), 56.7 (q), 99.9 (d), 105.6 (d), 115.1 (s), 117.9 (d), 121.7, 123.9 (d), 126.7 (d), 134.1 (d), 147.0 (s), 152.6 (s), 155.7 (s), 156.3 (s), 176.2 (s). HRMS (ESI) (m/z): $[M + 1]^+$ calcd for $C_{15}H_{13}O_4$, 257.0808; found, 257.0803.

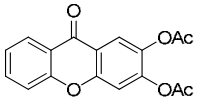
2,3-dihydroxy-*9H*-xanthen-9-one (S4)



S4

Compound **S3** (5 g, 19.51 mmol) and $AlCl_3$ (6.22 g, 46.83 mmol) were suspended in toluene (10 mL) and refluxed for 8 h under nitrogen atmosphere. After cooling down to room temperature, 20 mL conc. HCl and 80 mL ice water were carefully added to quench the reaction. The precipitate was filtered and washed with toluene. The residue was recrystallized from methanol and water (1:1, 40 mL). The product was obtained as a white solid (3.56 g, 80 %). ^{1}H NMR (300 MHz, D_6-DMSO) δ 6.90 (s, 1H), 7.40-7.43 (m, 2H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.77 (t, *J* = 7.5, 7.2 Hz, 1H), 8.12 (d, *J* = 7.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) 103.5 (d), 109.4 (d), 114.3 (s), 118.5 (d), 121.4 (s), 124.5 (d), 126.4 (d), 135.0 (d), 144.5 (s), 151.7 (s), 154.6 (s), 156.1 (s), 175.3 (s). *m*/*z* (EI^+, %) 228 (M^+, 100). HRMS (EI^+): calcd for $C_{13}H_8O_4$, 228.0423; found, 228.0418.

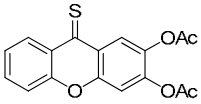
9-oxo-9H-xanthene-2,3-diyl diacetate (S5)



S5

2,3-Dihydroxy-xanthone **S4** (2.00 g, 8.76 mmol) was dissolved in pyridine (20 mL) and acetic anhydride (5 mL, 59 mmol) was slowly added and the mixture was stirred at room temperature overnight. The mixture was poured into water (100 mL) and the solid was collected via filtration. The product was obtained as a white solid (2.3 g, 84 %) after recrystallization from ethanol. ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 6H), 6.94 (s, 1H), 7.38-7.49 (m, 3H), 7.73 (t, *J* = 7.6, 8.0 Hz, 1H), 8.12 (s, 1H), 8.31 (d, *J* = 8.0 Hz, 1H). ^{13}C NMR (APT, 75 MHz, $CDCl_3$) 20.7 (q), 21.0 (q), 113.2 (d), 118.2 (d), 120.2 (s), 121.0 (d), 121.5 (s), 124.6 (d), 127.0 (d), 135.3 (d), 139.1 (s), 147.7 (s), 154.2 (s), 156.5 (s), 167.6 (s), 168.4 (s), 176.1 (s). *m*/*z* (EI^+, %) 312 (M^+, 8), 270 (21), 228 (100). HRMS (EI^+): calcd for $C_{17}H_{12}O_6$, 312.0634; found, 312.0627.

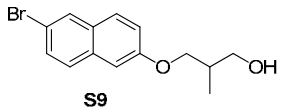
9-thioxo-9H-xanthene-2,3-diyl diacetate (S6)



S6

Ketone **S5** (2.00 g, 6.40 mmol) and Lawesson's reagent (3.76 g, 9.29 mmol) were suspended in THF (50 mL) and the mixture was stirred at room temperature for 24 h. TLC of the reaction mixture showed no evidence of starting material. Most of solvent was removed under reduced pressure. The mixture was filtered through a plug of silica (5 cm thick, 3 cm diameter). The silica was washed with CH_2Cl_2 until no green coloured material further eluted. Then the combined reaction mixture was concentrated in vacuo to give a dark blue solid (1.89 g, 90 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.36 (s, 6H), 7.38 (t, *J* = 6.8, 8.4 Hz, 1H), 7.48 (m, 2H), 7.77 (t, *J* = 6.8, 8.4 Hz, 1H), 8.53 (s, 1H), 8.70 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) 20.7 (q), 21.1 (q), 113.2 (d), 118.4 (d), 123.9 (d), 125.4 (d), 127.4 (s), 128.7 (s), 130.1 (d), 135.3 (d), 140.0 (s), 148.0 (s), 148.5 (s) , 150.7 (s), 167.5 (s), 168.5 (s), 203.1 (s). *m*/*z* (EI^+, %) 328 (M^+, 25), 244 (100). HRMS (EI^+): calcd for $C_{17}H_{12}O_5S$, 328.0405; found, 328.0392.

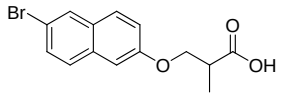
3-(6-bromonaphthalen-2-yloxy)-2-methylpropan-1-ol (S9)



S9

To a stirred solution of 6-bromo-2-naphthol **S7** (18 g, 80.7 mmol) in DMF (500 mL), K_2CO_3 (25 g, 0.18 mol) and compound **S8** (25 g, 102.3 mmol) were added, and the mixture was heated at reflux for 48 h. After cooling down to room temperature, the mixture was diluted in ethyl acetate and washed with an aqueous solution of HCl (10 %, 3 × 200 mL), saturated $NaHCO_3$ (200 mL), and brine, and dried (Na_2SO_4). After removal of the solvent under reduced pressure, the pure product which solidified upon standing was obtained after column chromatography (SiO_2, CH_2Cl_2/Ethyl acetate = 10:1, R_f = 0.56), as a white solid (16.7 g, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.09 (d, *J* = 6.8 Hz, 3H), 1.99 (s, 1H), 2.23-2.28 (m, 1H), 3.74 (d, *J* = 5.6 Hz, 2H), 4.04 (d, *J* = 6.0 Hz, 2H), 7.11 (s, 1H), 7.15 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.49 (dd, *J* = 8.8, 1.2 Hz, 1H), 7.57 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.8 Hz, 1H), 7.90 (s, 1H). ^{13}C NMR (APT, 100 MHz, $CDCl_3$) 13.9 (q), 35.9 (d), 66.0 (t), 71.2 (t), 107.0 (d), 117.3 (s), 120.1 (d), 128.6 (d), 128.7 (d), 129.9 (2d), 130.3 (s), 133.3 (s), 157.4 (s). *m*/*z* (EI^+, %) 294, 296 (M^+, 33), 222, 224 (100). HRMS (EI^+): calcd for $C_{14}H_{15}{}^{79}BrO_2$, 294.0255; found, 294.0240.

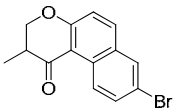
3-(6-bromonaphthalen-2-yl-oxy)-2-methylpropanoic acid (S10)



S10

CrO_3 (7 g, 70 mmol), H_2SO_4 (7 mL) and water (22 mL) were carefully mixed to give a red solution under ice bath cooling. To a stirred solution of compound **S9** (15 g, 50.82 mmol) in acetone (250 mL), the freshly produced Jones reagent was added in 2 h, after which stirring was continued for another 3 h. The mixture was acidified by addition of aqueous HCl (10 %) and extracted with ethyl acetate (3 × 200 mL). The organic extracts were washed with brine, dried (Na_2SO_4), and the solvent was removed under reduced pressure. The pure product was obtained after column chromatography (SiO_2, first CH_2Cl_2, then CH_2Cl_2/Ethyl acetate = 5:1, R_f = 0.60) as a white solid (11.8 g, 75 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40 (d, *J* = 6.8 Hz, 3H), 3.04-3.09 (m, 1H), 4.14 (dd, *J* = 8.4, 6.0 Hz, 1H), 4.04 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.11 (s, 1H), 7.16 (dd, *J* = 9.2, 1.6 Hz, 1H), 7.50 (d, *J* = 8.8 Hz, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.91 (s, 1H). ^{13}C NMR (APT, 100 MHz, $CDCl_3$) 14.1 (q), 39.9 (d), 69.5 (t), 107.2 (d), 117.5 (s), 120.1 (d), 128.6 (d), 128.8 (d), 129.9 (2d), 130.4 (s), 133.2 (s), 157.0 (s), 180.6 (s). *m*/*z* (EI^+, %) 308, 310 (M^+, 70), 222, 224 (100). HRMS (EI^+): calcd for $C_{14}H_{13}{}^{79}BrO_3$, 308.0048; found, 308.0057.

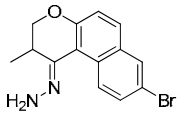
8-bromo-2,3-dihydro-2-methylbenzo[f]chromen-1-one (S11)



S11

Acid **S10** (10 g, 32.3 mmol) was dissolved in CH_2Cl_2 (50 mL), and $SOCl_2$ (10 mL) and a drop of DMF were added. The mixture was heated at reflux for 1 h. Solvent and excess $SOCl_2$ were removed under reduced pressure. The residue was dissolved again in CH_2Cl_2 (100 mL) and cooled to 0 °C. $AlCl_3$ (4.72 g, 35.5 mmol) was added to the mixture in 1 h at 0 °C. The mixture was stirred for an additional 0.5 h at 0 °C. Subsequently the dark solution was allowed to warm to room temperature slowly, followed by addition of 20 mL conc. HCl and 70 mL ice water to quench the reaction. After extraction with CH_2Cl_2 (3 × 50 mL), the organic layer was combined and dried with Na_2SO_4. After filtration, the solvent was removed under reduced pressure and the pure product was obtained after column chromatography (SiO_2, toluene, R_f = 0.50) as a white solid (8.0 g, 85 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (d, *J* = 8.4 Hz, 3H), 2.95 (m, 1H), 4.24 (t, *J* = 11.2, 9.8 Hz, 1H), 4.62 (dd, *J* = 11.2, 5.2 Hz, 1H), 7.12 (d, *J* = 9.2 Hz, 1H),7.68 (dd, *J* = 9.2, 2.4 Hz, 1H), 7.81 (d, *J* = 8.8 Hz, 1H), 7.89 (s, 1H), 9.37 (d, *J* = 8.8 Hz, 1H). ^{13}C NMR (APT, 100 MHz, $CDCl_3$) 11.4 (q), 41.4 (d), 72.3 (t), 112.2 (s), 118.7 (s), 120.2 (d), 127.9 (d), 130.4 (d), 130.5 (s), 130.8 (s), 132.6 (d), 136.1(d), 163.7 (s), 196.0 (s). *m*/*z* (EI^+, %) 290, 292 (M^+, 65), 248, 250 (100). HRMS (EI^+): calcd for $C_{14}H_{11}{}^{79}BrO_2$, 289.9942; found, 289.9913.

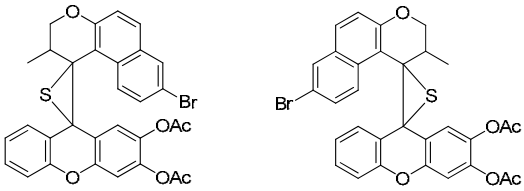
1-(8-bromo-2,3-dihydro-2-methylbenzo[f]chromen-1-ylidene)hydrazine (S12)



S12

Ketone **S11** (2 g, 6.8 mmol) was dissolved in ethanol (10 mL), and hydrazine monohydrate (3 mL) and a catalytic amount of *p*-toluenesulfonic acid monohydrate were added. Subsequently the mixture was heated at reflux for three days. After cooling down to room temperature, water (5 mL) was added. The precipitate formed at 0 °C was filtered and washed with cold methanol and water (1:1, in total 30 mL). The pure product was obtained as a white solid (1.47 g, 70 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.29 (d, *J* = 6.8 Hz, 3H), 3.27 (m, 1H), 4.26 (m, 2H), 5.50 (s, 2H), 7.11 (s, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 7.56 (m, 2H), 7.87 (s, 1H), 9.48 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (APT, 100 MHz, $CDCl_3$) 13.2 (q), 27.1 (d), 70.6 (t), 112.2 (s), 117.8 (s), 120.1 (d), 129.6 (d), 130.1 (d), 130.4 (d), 130.6 (d), 131.9 (s), 148.5 (s), 155.5 (s). HRMS (ESI): $[M + 1]^+$ calcd for $C_{14}H_{14}{}^{79}BrN_2O$, 305.0284; found, 305.0280.

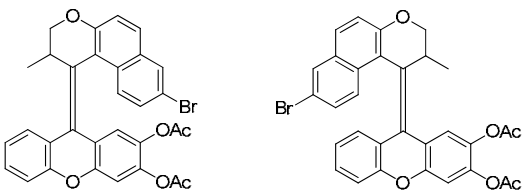
Episulfides *cis*-S13 and *trans*-S13



cis-**S13** *trans*-**S13**

To a solution of hydrazone **S12** (1 g, 3.28 mmol) in DMF (10 mL), stirred at 0 °C, was added a solution of [bis(acetoxy)iodo]benzene (1.26 g, 3.94 mmol) in DMF (10 mL). After 20 sec of stirring, a solution of thioketone **S6** (0.86 g, 2.62 mmol) in CH_2Cl_2 (20 mL) was added. The mixture was stirred at 0 °C for another two hours and then allowed to warm to room temperature overnight, followed by dilution with EtOAc. The organic layer was washed with water and brine, dried (Na_2SO_4) and concentrated under reduced pressure. Column chromatography (SiO_2, CH_2Cl_2, R_f = 0.68) yielded 0.96 g (61 %) of a yellow solid, which by ^{1}H NMR was identified as as a 1:1.2 mixture of *cis*/*trans* isomers. An analytical sample was obtained by flash chromatography (SiO_2; Heptane/EtOAc = 4/1) for characterization. *m*/*z* (EI^+, %) 602, 604 (M^+, 100), 570, 572 (88). HRMS (EI^+): calcd for $C_{31}H_{23}{}^{79}BrO_6S$, 602.0399; found, 602.0375. *Cis*-**S13** (R_f = 0.65): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (d, *J* = 6.8 Hz, 3H), 2.03 (s, 3H), 2.13 (s, 3H), 2.40 (m, 1H), 3.50-3.63 (m, 2H), 6.51 (s, 1H), 6.78 (s, 1H), 6.82 (d, *J* = 8.8 Hz, 1H), 7.20 (m, 2H), 7.39 (m, 2H), 7.55 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 8.87 (d, *J* = 9.6 Hz, 1H). ^{13}C NMR (APT, 100 MHz, $CDCl_3$) 19.4 (q), 20.3 (q), 20.8 (q), 39.2 (d), 53.1 (s), 59.4 (s), 72.6 (t), 110.8 (d), 116.0 (s), 116.6 (s), 116.7 (d), 119.0 (d), 120.1 (s), 120.9 (s), 122.1 (d), 123.4 (d), 124.4 (d), 128.9 (d), 129.1 (d), 129.2 (d), 129.4 (d), 131.0 (d), 131.3 (s), 133.1 (s), 136.7 (s), 141.7 (s), 151.4 (s), 155.4 (s), 156.4 (s), 167.5 (s), 167.8 (s). *Trans*-**S13** (R_f = 0.60): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (d, *J* = 6.8 Hz, 3H), 2.33 (s, 6H), 2.47 (m, 1H), 3.53 (dd, *J* = 6.8, 2.8 Hz, 1H), 3.73 (m, 1H), 6.28 (dd, *J* = 9.2, 6.8 Hz, 1H), 6.70-6.90 (m, 4H), 7.13 (s, 1H), 7.30 (d, *J* = 8.8 Hz, 1H), 7.57 (m, 2H), 7.76 (s, 1H), 8.89 (d, *J* = 9.2 Hz, 1H). ^{13}C NMR (APT, 100 MHz, $CDCl_3$) 19.7 (q), 20.9 (2q), 39.8 (d), 53.1 (s), 59.4 (s), 72.9 (t), 111.8 (s), 115.7(d), 117.1 (s), 117.2 (s), 119.1 (d), 120.4 (s), 120.7 (s), 122.6 (d), 123.6 (d), 124.6 (d), 127.8 (d), 128.4 (d), 128.5 (d), 129.2 (d), 130.5 (d), 131.1 (s), 133.1 (s), 137.5 (s), 142.6 (s), 153.1 (s), 153.9 (s), 156.3 (s), 168.1 (s), 168.8 (s).

Overcrowded alkenes *cis*-S14 and *trans*-S14

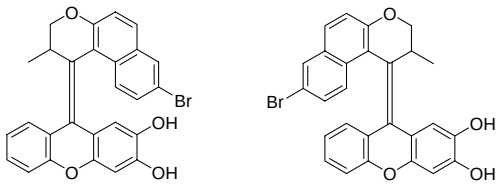


cis-**S14** *trans*-**S14**

A solution of a mixture of episulfides *cis*-**S13** and *trans*-**S13** (400 mg, 0.66 mmol) and PPh_3 (500 mg,

1.91 mmol) in *p*-xylene was heated at reflux overnight. The solvent was removed by distillation in vacuo, and the mixture was purified by flash chromatography (SiO_2, CH_2Cl_2, R_f = 0.67) to give 340 mg of alkene (95%) as a 1:1.2 mixture of *cis*-**S14** and *trans*-**S14**. An analytical sample was obtained by flash chromatography (SiO_2, Heptane/EtOAc = 4/1). *m*/*z* (EI^+, %) 528, 530 (66), 570, 572 (M^+, 100). HRMS (EI^+): calcd for $C_{31}H_{23}{}^{79}BrO_6$, 570.0678; found, 570.0662. *Cis*-**S14** (R_f = 0.63): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 (d, *J* = 6.8 Hz, 3H), 1.96 (s, 3H), 2.20 (s, 3H), 4.08 (m, 1H), 4.54 (d, *J* = 10.8 Hz, 1H), 4.73 (dd, *J* = 3.6, 10.4 Hz, 1H), 6.29 (s, 1H), 7.07 (s, 1H), 7.11 (d+s, 2H), 7.20-7.40 (m, 4H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.80 (s, 1H). ^{13}C NMR (APT, 100 MHz, $CDCl_3$) 17.1 (q), 20.5 (q), 20.8 (q), 31.1 (d), 74.9 (t), 111.9 (d), 115.2 (s), 117.1 (s), 117.3 (d), 119.2 (d), 121.0 (s), 122.1 (d), 123.7 (d), 124.7 (s), 125.2 (s), 126.0 (d), 127.2 (d), 128.6 (d), 129.0 (s), 129.3, 129.4, 130.0, 130.4 (s), 130.9 (s), 137.8 (s), 141.5 (s), 151.6 (s), 154.3 (s), 155.0 (s), 167.9 (s), 168.0 (s). *Trans*-**S14** (R_f = 0.57): ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.95 (d, *J* = 6.4 Hz, 3H), 2.34 (s, 6H), 4.03 (m, 1H), 4.55 (d, *J* = 10.4 Hz, 1H), 4.72 (dd, *J* = 4.4, 10.8 Hz, 1H), 6.35 (dd, *J* = 7.6 Hz, 1H), 6.45 (d, *J* = 7.6 Hz, 1H), 6.96-7.02 (m, 2H), 7.13 (dd, *J* = 8.8, 9.2 Hz, 2H), 7.19 (s, 1H), 7.31 (s, 1H), 7.58 (d, *J* = 8.8 Hz, 1H), 7.75 (d, *J* = 1.6 Hz, 1H). ^{13}C NMR (APT, 100 MHz, $CDCl_3$) 17.1 (q), 20.9 (q), 21.0 (q), 31.0 (d), 74.8 (t), 112.3 (d), 115.7 (s), 116.7 (s), 116.8 (d), 119.2 (d), 120.9 (s), 121.4 (d), 123.3 (d), 123.8 (s), 125.8 (s), 126.2 (d), 128.1 (d), 128.3 (d), 128.9 (d), 128.9 (s), 129.3 (d), 129.8 (d), 130.3 (s), 131.0 (s), 137.7 (s), 141.5 (s), 153.0 (s), 153.7 (s), 154.3 (s), 168.3 (s), 168.7 (s).

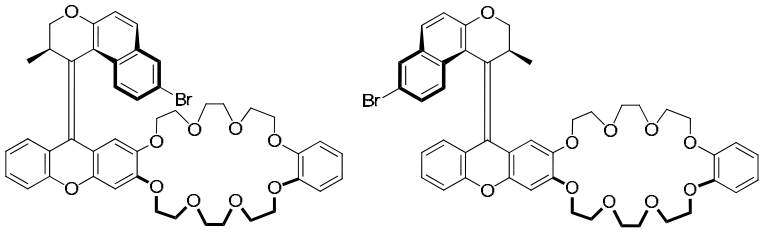
Motor S15



cis-**S15** *trans*-**S15**

A solution of LiOH (40 mg, 1.67 mmol) in water and MeOH (1:1, 4 mL in total) was added to a solution of *cis*/*trans*-**S14** (300 mg, 0.525 mmol) in THF (20 mL). This mixture was stirred under inert atmosphere for 4 h, then acidified to pH 2 with dilute aqueous HCl and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with water (2 × 5 mL), brine (3 mL), dried with Na_2SO_4. After filtration, the solvent was removed in vacuo to give 220 mg (85 %) of a red solid as a mixture of *cis* and *trans* isomer and some impurities which could not be removed at this stage. The product was used directly for the next step.

Bromo-substituted crown ether motor *cis*/*trans* S17

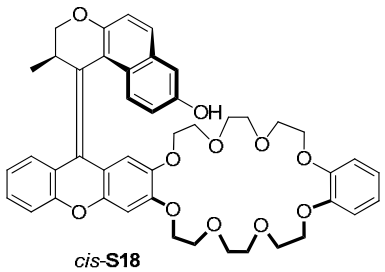


cis-**S17** *trans*-**S17**

A solution of dihydroxy motor **S15** (100 mg, 0.205 mmol) in dry DMF (15 mL) was added under N_2 atmosphere over 30 min to a suspension of caesium carbonate (210 mg, 0.63 mmol) in dry DMF (10 mL), while the temperature was raised to 100 ° C. After 15 min a solution of ditosylate **S16** (143 mg, 0.21 mmol) in dry DMF (10 mL) was added and the reaction mixture was then heated at 100 ° C for 2 d. After cooling to room temperature, the suspension was filtered and the solid was washed with DMF. The solvent was removed under reduced pressure. The resulting brown residue was partitioned between EtOAc (50 mL) and H_2O (30 mL). The aqueous phase was extracted once more with EtOAc (50 mL) and the combined organic extracts were washed with water (2 × 20 mL), brine (15 mL), dried (Na_2SO_4) and the solvent was removed in vacuo. The product was purified by flash chromatography (SiO_2, neat EtOAc, R_f = 0.70) to give a mixture of *cis*/*trans* **S17** (2.5:1) as a yellow sticky oil which solidified upon standing (50 mg, 30 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, *J* = 6.6 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H), 2.78 (m, 1H), 3.14 (m, 1H), 3.35-3.50 (m, 2H), 3.62 (m, 2H), 3.73-4.25 (m, 44H), 4.50 (m, 2H), 4.70 (m, 2H), 6.10 (s, 1H), 6.32 (dd, *J* = 6.6 Hz, 1H), 6.69 (s, 1H), 6.84-6.98 (m, 10H), 7.06-7.38 (m, 12H), 7.52-7.58 (m, 4H), 7.78 (m, 2H). ^{13}C NMR (APT, 125 MHz, $CDCl_3$) 17.1 (q), 17.2 (q), 31.4 (d),

31.6 (d), 63.9 (t), 67.8 (t), 69.1 (t), 69.2 (t), 69.5 (t), 69.6 (2 × t), 69.7 (t), 69.8 (t), 69.9 (2 × t), 70.1 (t), 70.2 (3 × t), 70.4 (t), 70.9 (t), 71.1 (2 × t), 71.2 (t), 71.4 (t), 71.5 (2 × t), 71.6 (t), 74.9 (t), 75.1 (t), 102.7 (2 × d), 113.8 (d), 114.3 (2 × d), 114.4 (d), 114.9 (d), 115.2 (d), 115.4 (d), 116.3 (s), 116.5 (s), 116.6 (d), 116.9 (2 × s), 117.2 (d), 117.4 (s), 117.8 (s), 119.3 (d), 119.7 (d), 121.7 (3 × d), 122.0 (d), 121.3 (s), 122.8 (d), 123.1 (d), 125.2 (2 × s), 126.1 (s), 126.5 (d), 126.9 (d), 127.4 (d), 127.9 (s), 127.9 (d), 128.1 (d), 128.3 (s), 128.5 (d), 128.7 (d), 128.8 (d), 128.9 (d), 129.1 (d), 129.3 (s), 129.8 (d), 130.3 (s), 130.4 (2 × s), 144.7 (s), 144.8 (s), 148.4 (s), 149.2 (2 × s), 149.3 (2 × s), 149.4 (s), 150.0 (s), 150.5 (s), 153.8 (s), 154.1 (s), 155.0 (s), 155.3 (s). *m*/*z* (ESI) 847.4, 849.4 (M + Na)$^+$. HRMS (ESI): calcd for $C_{45}H_{45}O_{10}{}^{79}BrNa$, 847.2088; found, 847.2073.

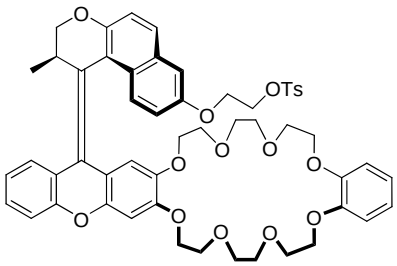
Motor *cis*-S18



cis-**S18**

Following the general procedure described by Buchwald and coworkers for hydroxylation.[3] In a sealed glass vial under N_2 was placed $Pd_2(dba)_3$ (11.28 mg, 12.32 μmol), *tert*-butyl X-phos ligand (10.46 mg, 24.64 umol), KOH (69 mg, 1.232 mmol), alkene *cis*/*trans* **S17** (100 mg, 0.123 mmol), water (3 mL) and dioxane (6 mL). The reaction mixture was heated at reflux for 36 h. After being cooled to room temperature, the mixture was acidified to pH 2 with dilute aqueous HCl and extracted with EtOAc (3 × 20 mL). The combined organic extracts were washed with water (2 × 20 mL), brine (15 mL), dried (Na_2SO_4) and the solvent was removed in vacuo. The product was purified by flash chromatography (SiO_2, first neat EtOAc, then acetone) to give *cis*-**S18** as yellow sticky oil which solidified upon standing (68.5 mg, 80 %). The *trans* form was observed in the crude product by ^{1}H NMR in a very small amount (<5 %) and eliminated by column chromatography. ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.99 (d, J = 7.0 Hz, 3H), 2.75 (m, 1H), 3.22 (m, 1H), 3.34 (m, 1H), 3.46 (m, 1H), 3.61 (m, 2H), 3.70-4.25 (m, 19H), 4.49 (d, J = 10.0 Hz, 1H), 4.72 (dd, J = 4.0, 10.0 Hz, 1H), 6.03 (s, 1H), 6.60 (d, J = 9.0 Hz, 1H), 6.71 (s, 1H), 6.92 (m, 4H), 7.00 (s, 1H), 7.03 (d, J = 9.0 Hz, 1H), 7.08 (d, J = 9.5 Hz, 1H), 7.20 (dd, J = 7.5, 8.0 Hz, 1H), 7.24-7.34 (m, 2H), 7.47 (d, J = 9.0 Hz, 1H), 7.51 (d, J = 7.5 Hz, 1H). ^{13}C NMR (APT, 125 MHz, $CDCl_3$) 17.5 (q), 31.3 (d), 69.5 (4 × t), 69.6 (2 × t), 69.9 (2 × t), 70.5 (t), 70.9 (t), 71.1 (t), 71.6 (t), 74.8 (t), 102.9 (d), 110.7 (d), 114.5 (d), 114.6 (2 × d), 114.8 (d), 116.2 (s), 117.1 (d), 118.6 (d), 118.7 (s), 120.8 (s), 122.0 (d), 122.1 (d), 123.1 (d), 125.4 (s), 125.8 (s), 126.4 (d), 127.2 (d), 128.10 (d), 128.15 (d), 129.4 (s), 130.4 (s), 144.7 (s), 148.7 (s), 148.8 (s), 148.9 (s), 149.0 (s), 152.1 (s), 152.7 (s), 155.2 (s). *m*/*z* (ESI) 780.3 (M + NH_4^+), 785.5 (M + Na)$^+$. HRMS (ESI): calcd for $C_{45}H_{50}NO_{11}$, 780.3378; found, 780.3415.

Motor *cis*-S20

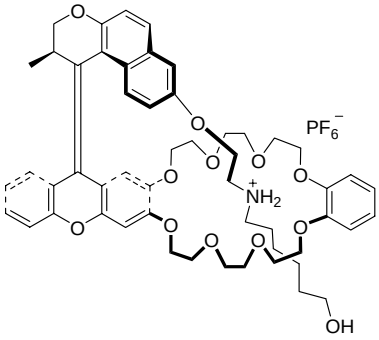


cis-**S20**

To a suspension of K_2CO_3 (0.25 g, 1.8 mmol) in CH_3CN (30 mL) was added *cis*-**S18** (100 mg, 0.131 mmol) and ditosylate **S19** (0.4 g, 1.1 mmol). The mixture was heated at reflux overnight. After cooling to room temperature, the suspension was filtered and the solid washed with CH_3CN. The solvent was removed under reduced pressure. The resulting brown residue was purified by flash chromatography (SiO_2, neat EtOAc, R_f = 0.64) to give *cis*-**S20** (<10% *trans*) as a yellow oil which solidified upon standing (100 mg, 79 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (d, J = 6.5 Hz, 3H), 2.42 (s, 3H), 2.78 (m, 1H), 3.10 (m, 1H), 3.32-3.45 (m, 2H), 3.62 (m, 2H), 3.70-4.20 (m, 21H), 4.34 (m, 2H), 4.45 (d, J = 10.0 Hz, 1H), 4.65 (dd, J = 4.5, 10.0 Hz, 1H), 6.14 (s, 1H), 6.59 (dd, J = 2.5, 9.0 Hz, 1H), 6.66 (s, 1H),

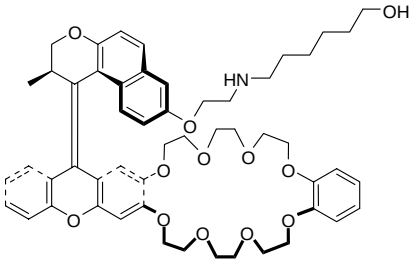
6.82-6.92 (m, 5H), 7.08 (m, 1H), 7.18 (dd, *J* = 7.5 Hz, 1H), 7.22-7.36 (m, 5H), 7.50 (d, *J* = 9.0 Hz, 1H), 7.55 (d, *J* = 7.5 Hz, 1H), 7.79 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (APT, 125 MHz, $CDCl_3$) 17.4 (q), 21.9 (q), 32.0 (d), 65.8 (t), 68.5 (t), 69.4 (t), 69.6 (3t), 69.7 (t), 69.8 (t), 70.1 (2 × t), 71.1 (t), 71.3 (t), 71.4 (t), 71.5 (t), 74.8 (t), 102.5 (d), 107.8 (d), 113.5 (d), 114.4 (2 × d), 116.7 (s), 117.2 (d), 118.0 (s), 118.4 (d), 119.0 (d), 121.7 (2 × d), 122.1 (s), 123.1 (d), 125.3 (s), 126.7 (d), 126.8 (s), 127.6 (d), 128.3 (2 × d), 128.4 (d), 128.8 (d), 129.9 (s), 130.1 (2 × d), 133.2 (s), 144.7 (s), 145.1 (s), 148.2 (s), 148.9 (s), 149.2 (2 × s), 152.5 (s), 154.3 (s), 154.9 (s). *m*/*z* (ESI) 983.4 $(M + Na)^+$. HRMS (ESI): calcd for $C_{54}H_{56}O_{14}NaS$, 983.3283; found, 983.3322.

Motor *cis*-1-H·PF$_6$



To a suspension of K_2CO_3 (0.125 g, 0.9 mmol) in CH_3CN (30 mL) was added *cis*-**S20** (100 mg, 0.104 mmol) and 6-amino-1-hexanol (0.2 g, 1.7 mmol). The mixture was heated at reflux overnight. After cooling down to room temperature, the suspension was filtered and the solid washed with CH_3CN. The solvent was removed under reduced pressure. The residue was dissolved in EtOAc (30 mL) and washed with brine (3 × 20 mL). The organic layer was dried and the solvent was removed under reduced pressure. The residue was dissolved in acetone (20 mL) and water (5 mL), and HCl (0.5 mL, 1M aqueous solution, 0.5 mmol) were added. NH_4PF_6 (1.5 g, 9.2 mmol) in H_2O (5 mL) was added and the mixture was stirred for a further 10 min. Volatile components were removed under reduced pressure whereupon the residue was diluted with H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 20 mL). The organic extracts were concentrated and the product was purified by flash chromatography (SiO_2, CH_2Cl_2/methanol = 100/6, R_f = 0.45) to yield *cis*-**1**-H·PF$_6$ as a yellow oil which solidified upon standing (54 mg, 0.023 mmol, 50 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.04 (d, *J* = 6.5 Hz, 3H), 1.32 (m, 4H), 1.43 (m, 2H), 1.48-1.68 (m, 2H), 2.95 (dd, *J* = 10.0, 9.5 Hz, 1H), 3.15 (d, *J* = 10.5 Hz, 1H), 3.20-3.58 (m, 7H), 3.70-4.35 (m, 23H), 4.50 (dd, *J* = 10.5, 7.0 Hz, 1H), 4.61 (d, *J* = 10.5 Hz, 1H), 4.81 (dd, *J* = 10.0, 4.0 Hz, 1H), 5.72 (s, 1H), 6.50 (d, *J* = 9.0 Hz, 1H), 6.75 (s, 1H), 6.92-7.03 (m, 5H), 7.16 (d, *J* = 8.5 Hz, 1H), 7.24 (dd, *J* = 7.0, 8.0 Hz, 1H), 7.28 (d, *J* = 7.5 Hz, 1H), 7.32 (m, 2H), 7.50 (d, *J* = 7.0 Hz, 1H), 7.55 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (APT, 125 MHz, CD_2Cl_2) 11.6 (q), 20.1 (t), 21.1 (t), 21.3 (t), 24.7 (t), 27.0 (d), 41.6 (t), 44.1 (t), 57.0 (t), 59.5 (t), 60.4 (t), 62.2 (t), 63.8 (t), 64.9 (t), 64.9 (t), 65.3 (t), 65.4 (t), 65.6 (t), 65.8 (t), 66.2 (t), 66.3 (t), 69.6(t), 95.6 (d), 105.4 (d), 107.0 (d), 107.9 (d), 108.7 (d), 109.4 (d), 110.1 (s), 111.4 (d), 112.0 (s), 114.2 (d), 114.9 (s), 116.6 (d), 117.2 (d), 117.8 (d), 120.2 (s), 121.0 (s), 121.3 (d), 121.4 (d), 122.3 (d), 122.7 (d), 123.8 (s), 123.9 (s), 138.1 (s), 141.6 (s), 141.8 (s), 143.1 (s), 145.9 (s), 147.9 (s), 149.6 (s). HRMS (ESI) (*m*/z): $(M - PF_6)^+$ calcd for $C_{53}H_{64}NO_{12}$, 906.4423; found, 906.4415.

Motor stable *cis*-1

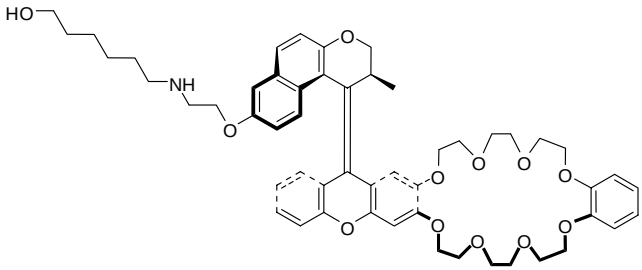


cis-**1**

To a suspension of *cis*-**1**-H·PF$_6$ (20 mg) in ethyl acetate (15 mL) was added a drop of DBU, and the mixture was stirred for 5 min. After washing with brine (3 × 10 mL), and drying over Na_2SO_4, the solvent was removed under vacuum to yield *cis*-**1** quantatively. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 0.96 (d,

J = 7.0 Hz, 3H), 1.37 (m, 4H), 1.50 (m, 2H), 1.69 (m, 2H), 2.63 (m, 2H), 2.77 (m, 1H), 2.95 (m, 2H), 3.09 (m, 1H), 3.34 (m, 2H), 3.41-4.18 (m, 25H), 4.45 (d, *J* = 10.0 Hz, 1H), 4.63 (dd, *J* = 9.5 Hz, 3.0 Hz, 1H), 6.18 (s, 1H), 6.67 (s, 1H), 6.73 (dd, *J* = 9.0 Hz, 2.0 Hz, 1H), 6.87 (m, 4H), 7.03 (d, *J* = 2.0 Hz, 1H), 7.09 (dd, *J* = 9.0 Hz, 1H), 7.22-7.35 (m, 4H), 7.57 (dd, *J* = 8.5 Hz, 5.5 Hz, 2H).

Motor stable *trans*-1



trans-**1**

Cis-**1** (10 mg) was dissolved in CH_2Cl_2 (5 mL, optical grade). The solution was irradiated at 365 nm at room temperature for 2 h. The solvent was removed under reduced pressure. Preparative TLC yielded 3 mg of *trans*-**1** with a trace amount of impurity. ^{1}H NMR (500 MHz, CD_2Cl_2) δ 0.94 (d, *J* = 6.5 Hz, 3H), 1.30-1.40 (m, 4H), 1.50 (m, 2H), 1.58 (m, 2H), 2.95 (m, 2H), 3.23 (m, 2H), 3.55 (t, *J* = 6.5 Hz, 2H), 3.70-4.22 (m, 25H), 4.46 (d, *J* = 10.5 Hz, 1H), 4.68 (dd, *J* = 4.0, 10.0 Hz, 1H), 6.30 (dd, *J* = 7.5, 8.0 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 6.85 (s, 1H), 6.87-6.93 (m, 5H), 7.00 (s, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 7.16 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H).

Characterization of *cis*-1-H·PF_6

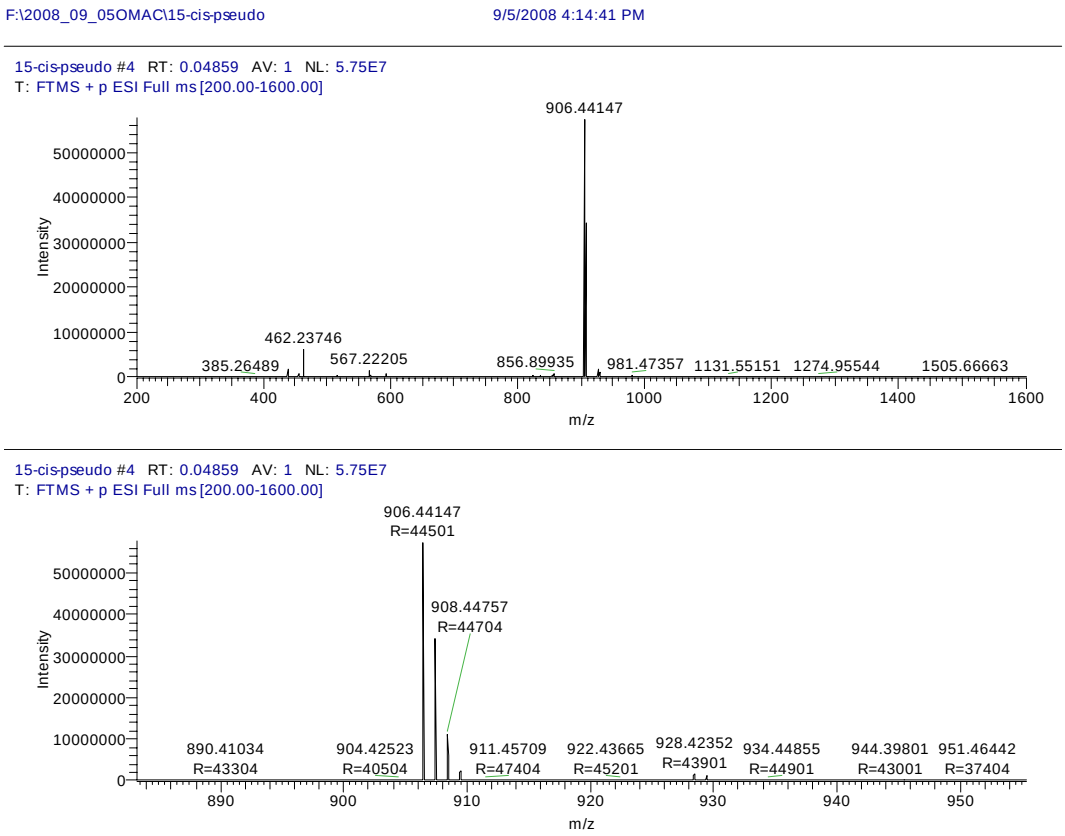


Figure S1. ESI-MS spectrum of *cis*-**1**-H•PF_6.

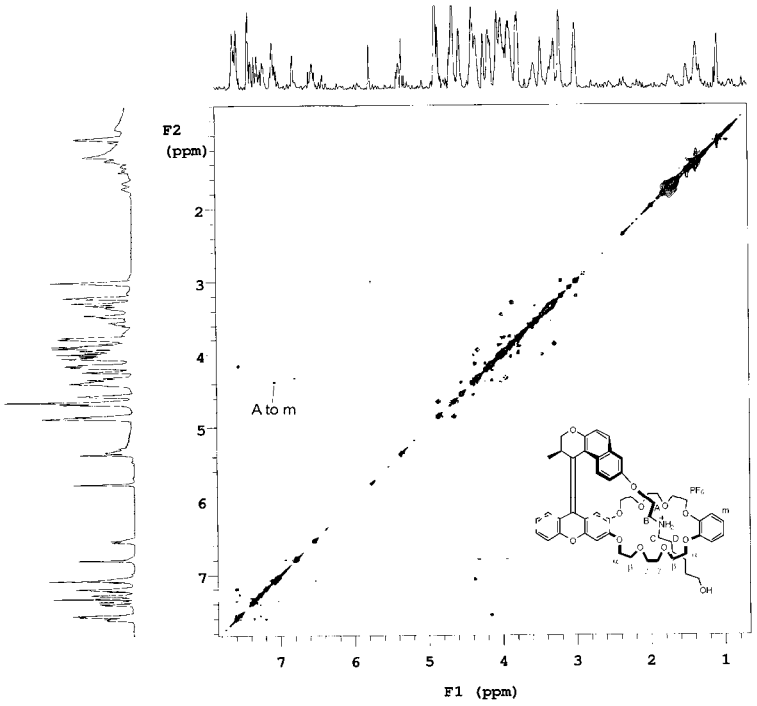


Figure S2. 2D Roesy NMR spectrum of *cis*-**1**-H•PF_6 in CD_2Cl_2.

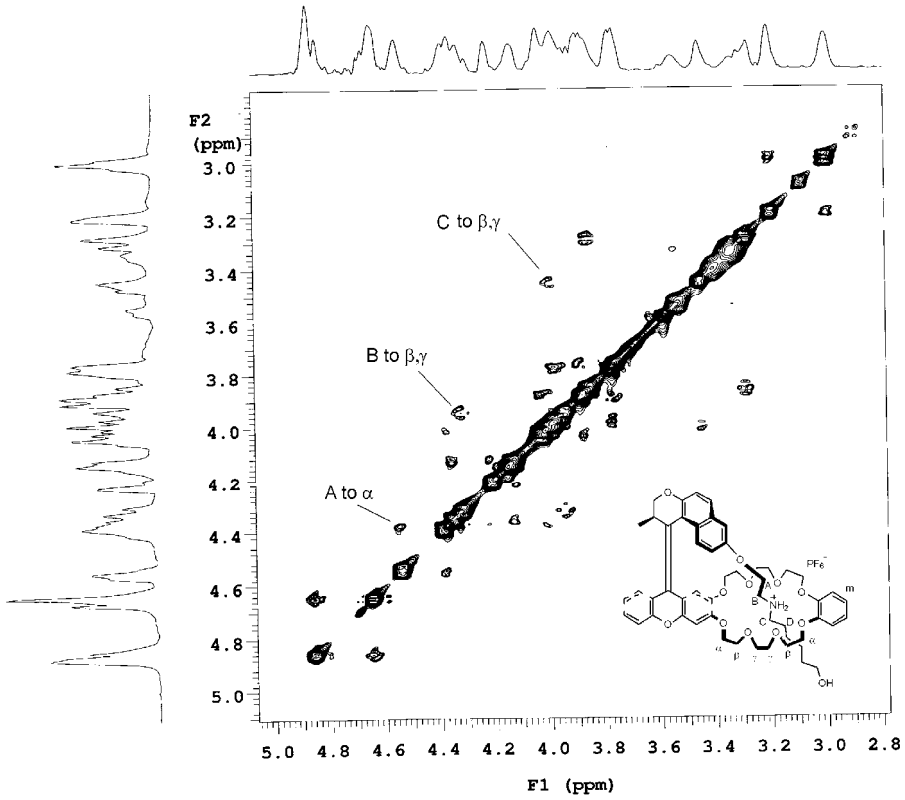


Figure S3. Partial 2D Roesy NMR spectrum of *cis*-**1**-H•PF_6 in CD_2Cl_2.

From the ^{1}H NMR spectra in different solvents, 2D ROESY NMR spectrum and ESI-MS spectra, we can conclude that *cis*-**1**-H·PF_6 has a pseudo-rotaxane structure.

Threading and dethreading movements

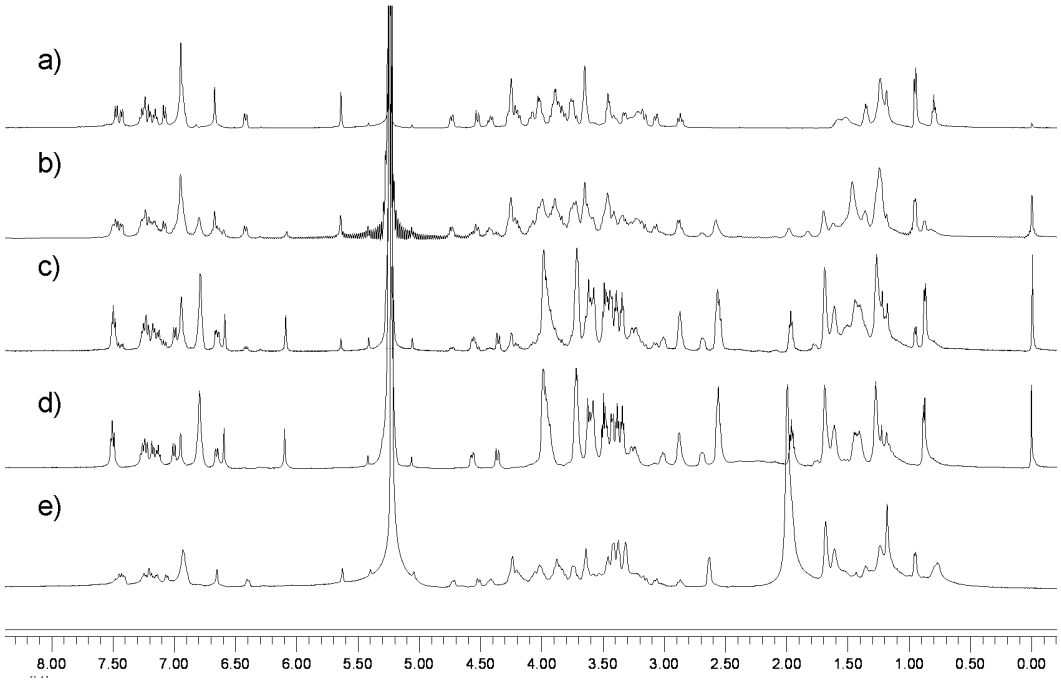


Figure S4. ^{1}H NMR spectra of *cis*-**1**-H•PF_6 in CD_2Cl_2: a) the original spectrum; b) after addition of 0.3 equivalent DBU base; c) after addition of 0.8 equivalent DBU base; d) after addition of 1.1 equivalent DBU base; e) futher addition of 1.3 equivalents CF_3COOH.

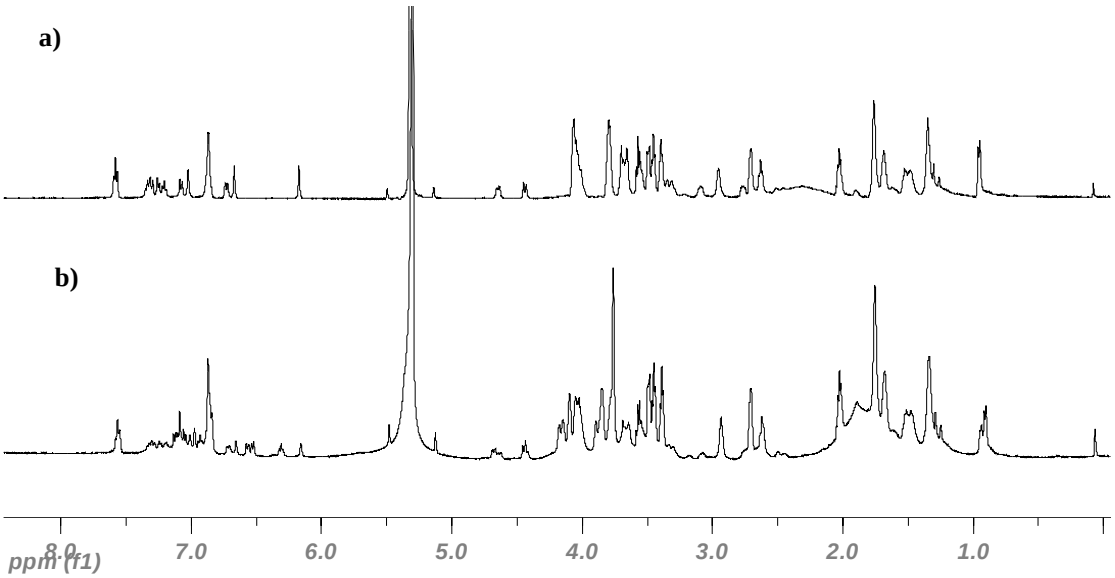


Figure S5. ^{1}H NMR spectra of *cis*-**1**-H•PF_6 in CD_2Cl_2: a) after addition of 1.1 equivalent DBU base; b) after irradiation at 365 nm at room temperature for 2 h.

Low-temperature ^{1}H NMR measurements

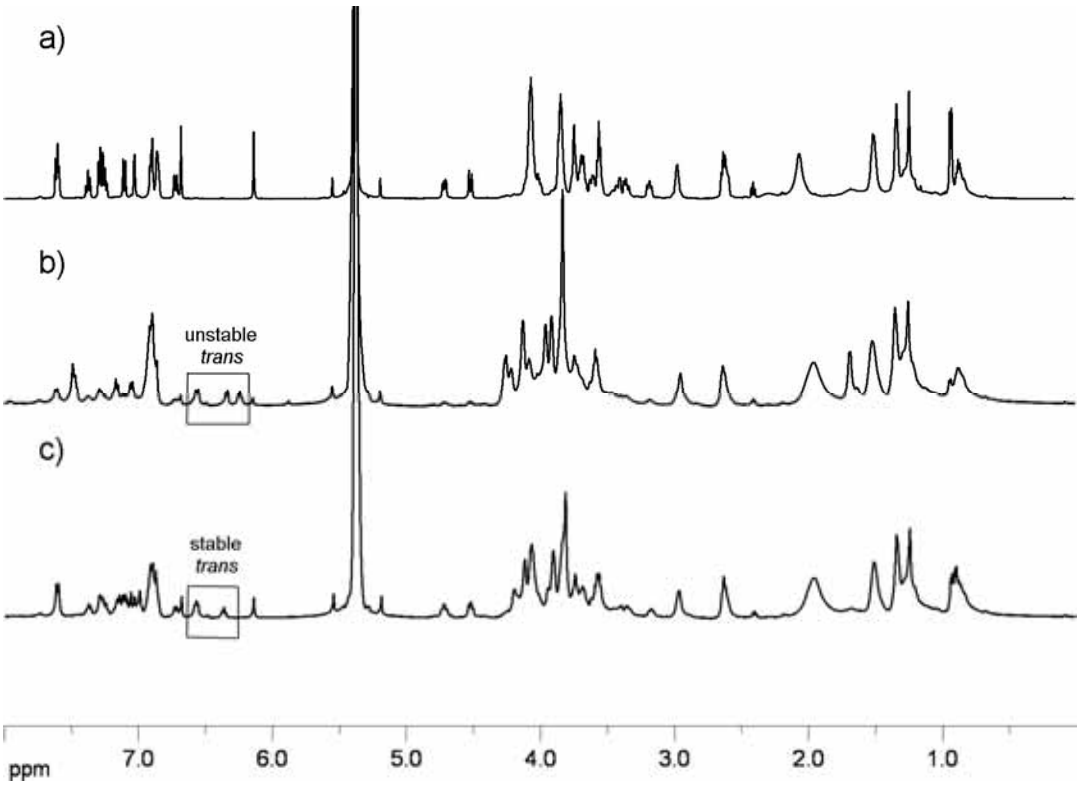


Figure S6. ^{1}H NMR spectra of *cis*-**1** in CD_2Cl_2: a) the original spectrum; b) after irradiation at 365 nm -25 ^{o} C for 3 h; c) the stable mixture after warming at room temperature for 20 min in the dark.

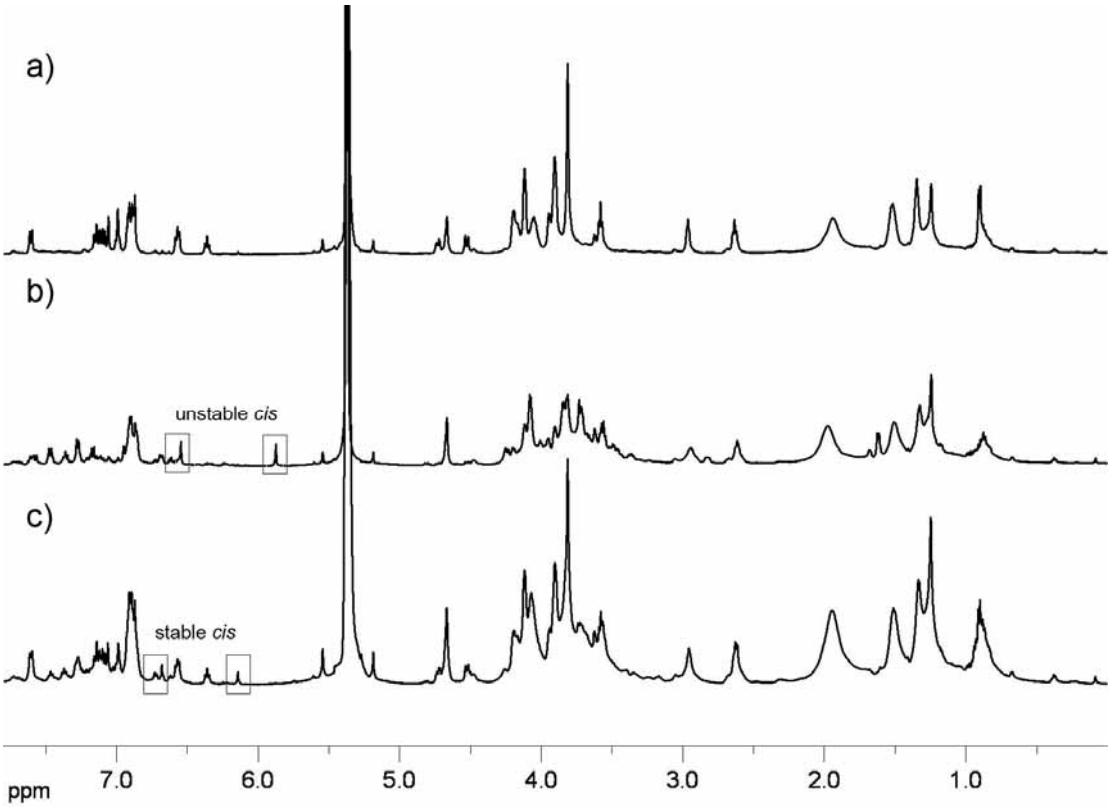


Figure S7. ^{1}H NMR spectra of *trans*-**1** in CD_2Cl_2: a) the original spectrum; b) after irradiation at 365 nm -25 ^{o} C for 3 h; c) the stable mixture after warming at room temperature for 20 min in the dark.

UV/Vis spectra of *cis*-1 and *trans*-1

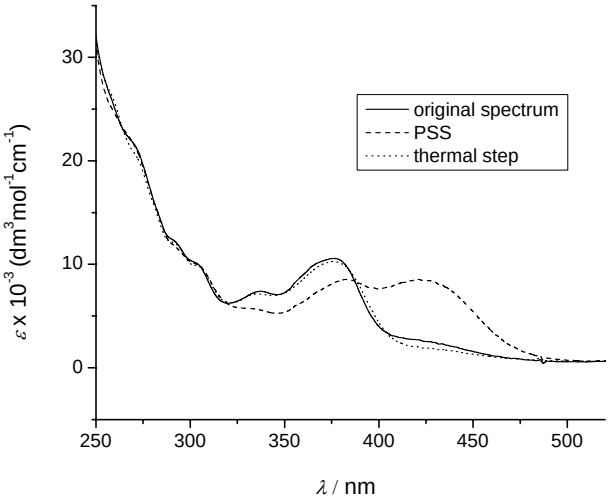


Figure S8. UV-vis spectra (CH_2Cl_2, -20 ^{o} C) of *cis*-**1** without DBU.

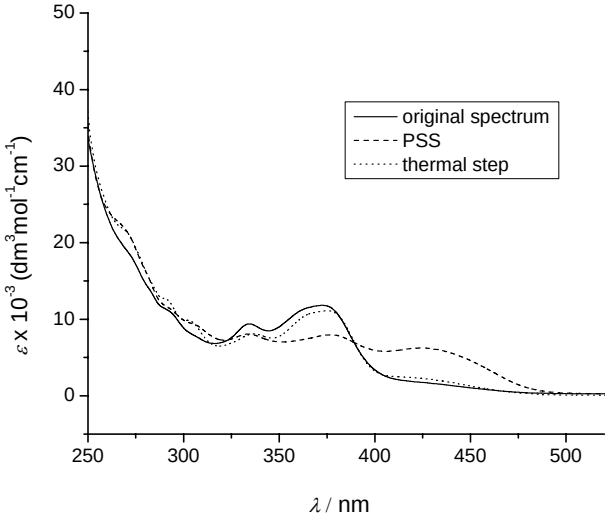


Figure S9. UV-vis spectra (CH_2Cl_2, -20 ^{o} C) of *trans*-**1** without DBU.

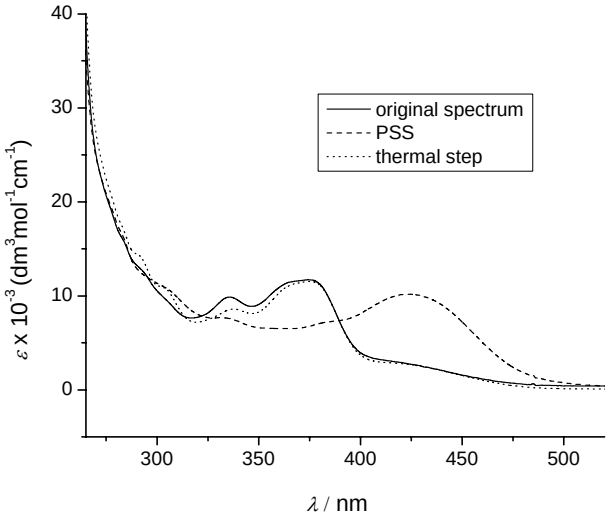
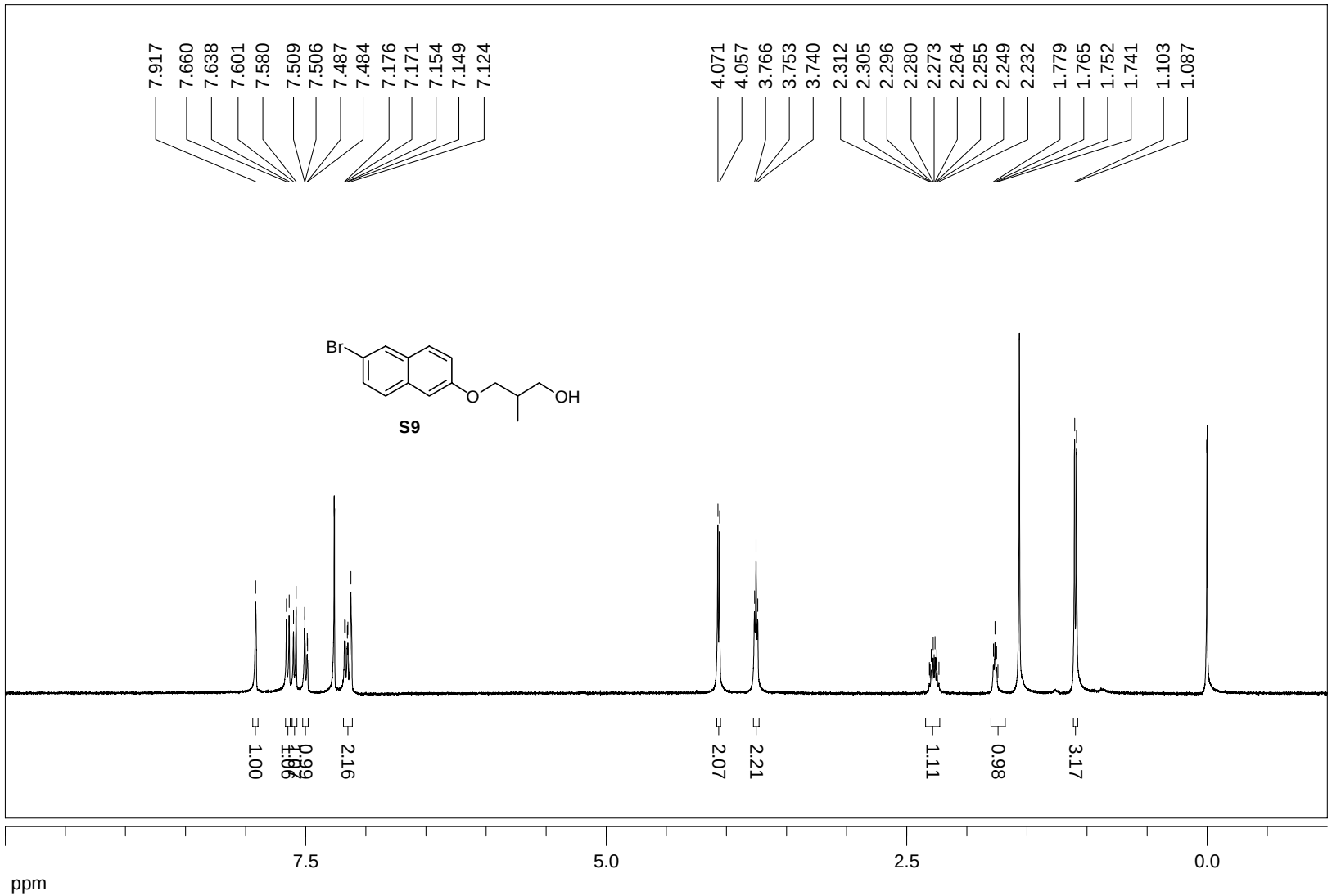


Figure S10. UV-vis spectra (CH_2Cl_2, -20 ^{o} C) of *trans*-**1** in the presence of 5 eq DBU.

References

1. D. Pijper, M. G. M. Jongejan, A. Meetsma, and B. L. Feringa, *J. Am. Chem. Soc.* **2008**, *130*, 4541 – 4552.
2. S. J. Cantrill, G. J. Youn, and J. F. Stoddart, *J. Org. Chem.* **2001**, *66*, 6857 – 6872.
3. K.W. Anderson, T. Ikawa, R.E. Tundel, S. L. Buchwald, *J. Am. Chem. Soc.* **2006**, *128*, 10694 – 10695.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7.149
7.124
4.071
4.057
3.766
3.753
3.740
2.312
2.305
2.296
2.280
2.273
2.264
2.255
2.249
2.232
1.779
1.765
1.752
1.741
1.103
1.087
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OH
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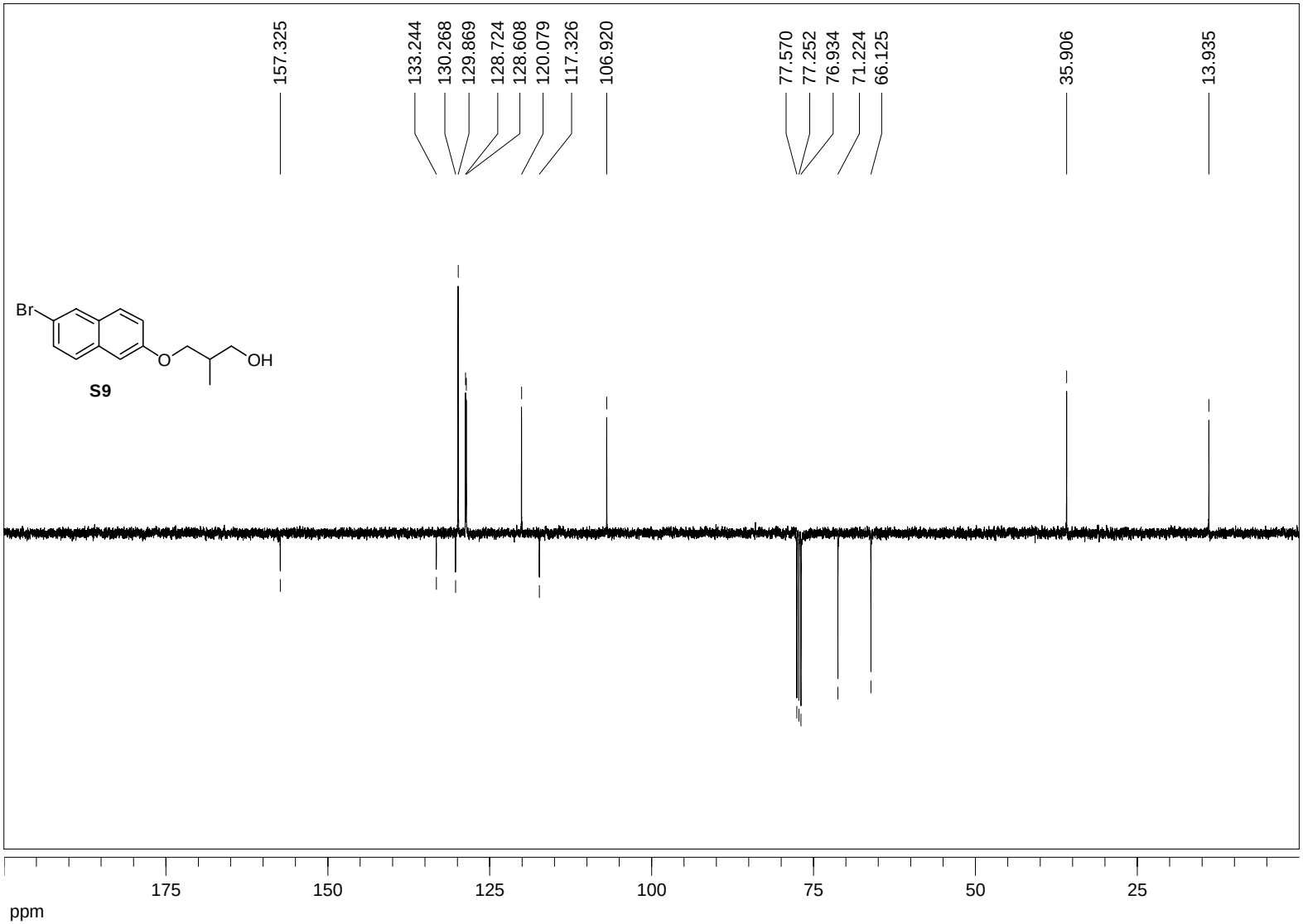
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75
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25
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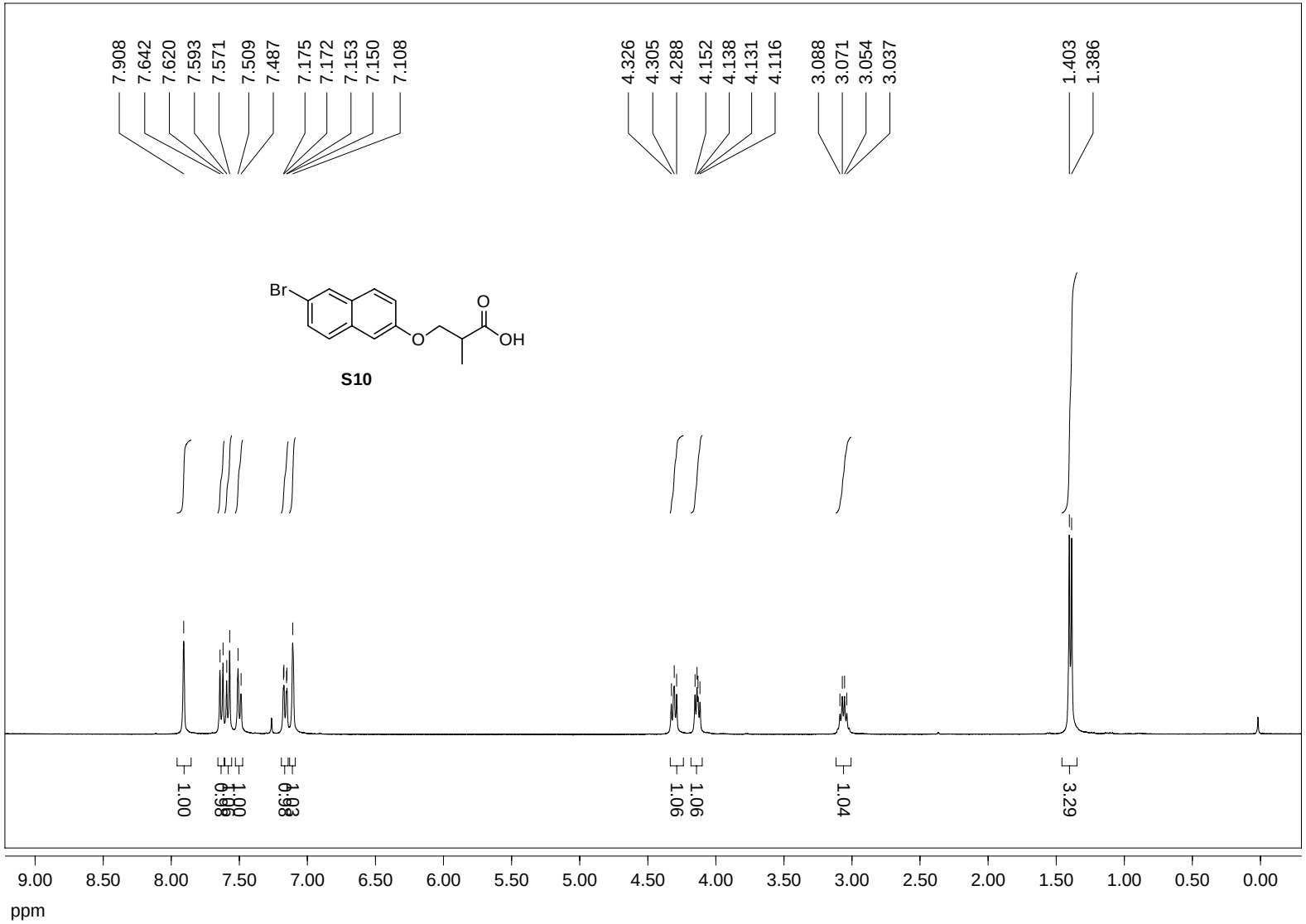
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O
O
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1.06
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3.29
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8.00
7.50
7.00
6.50
6.00
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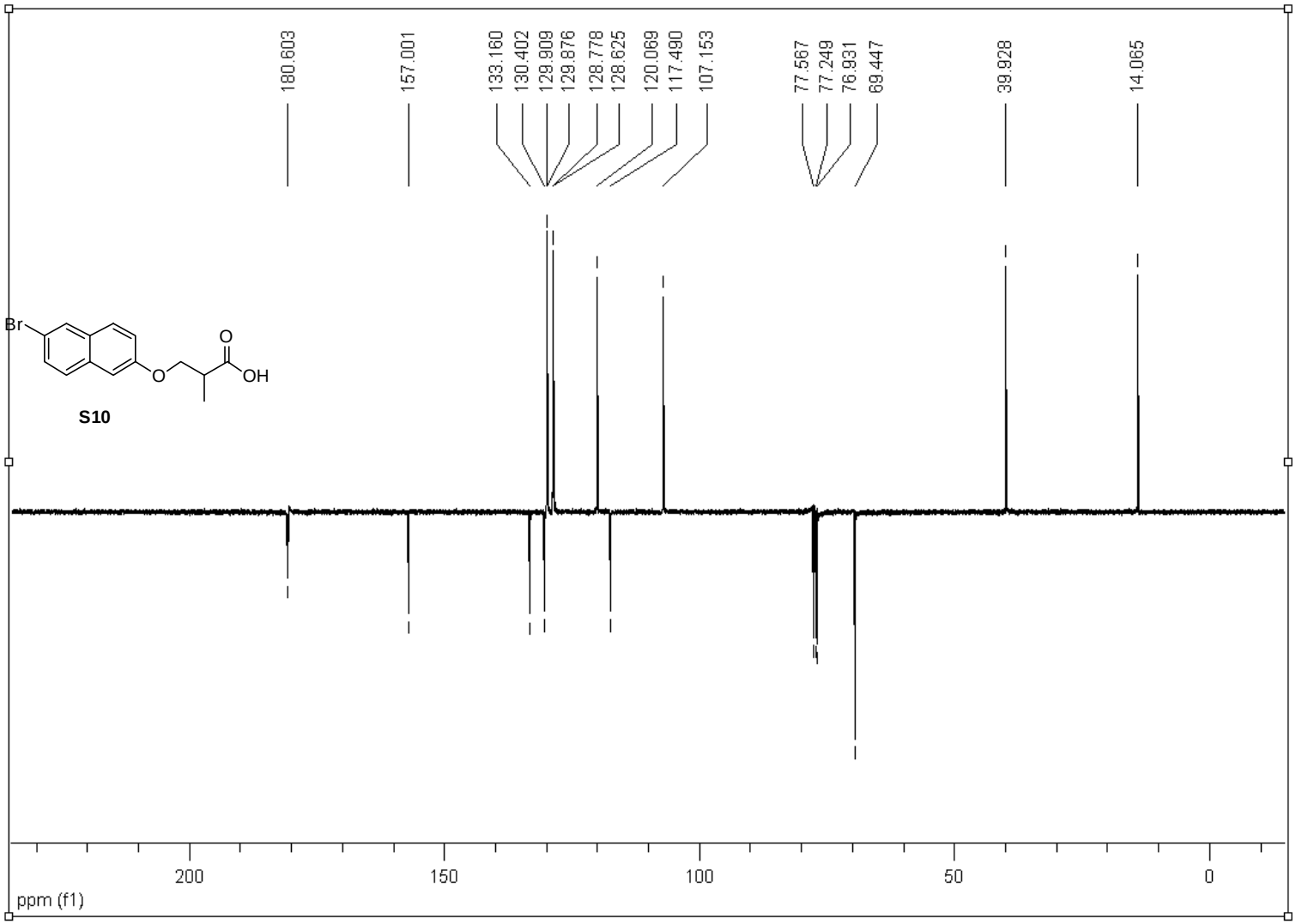
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O
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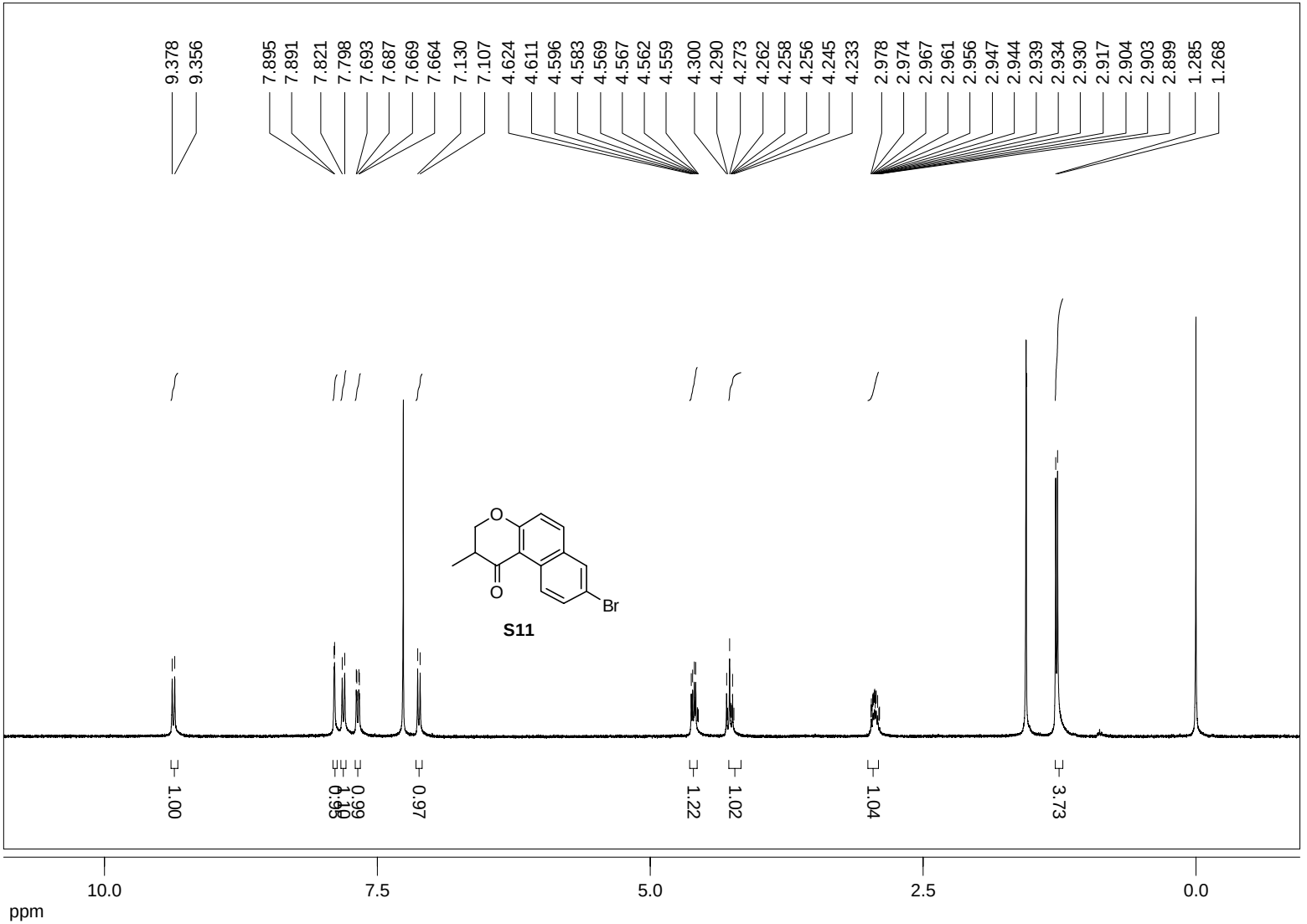
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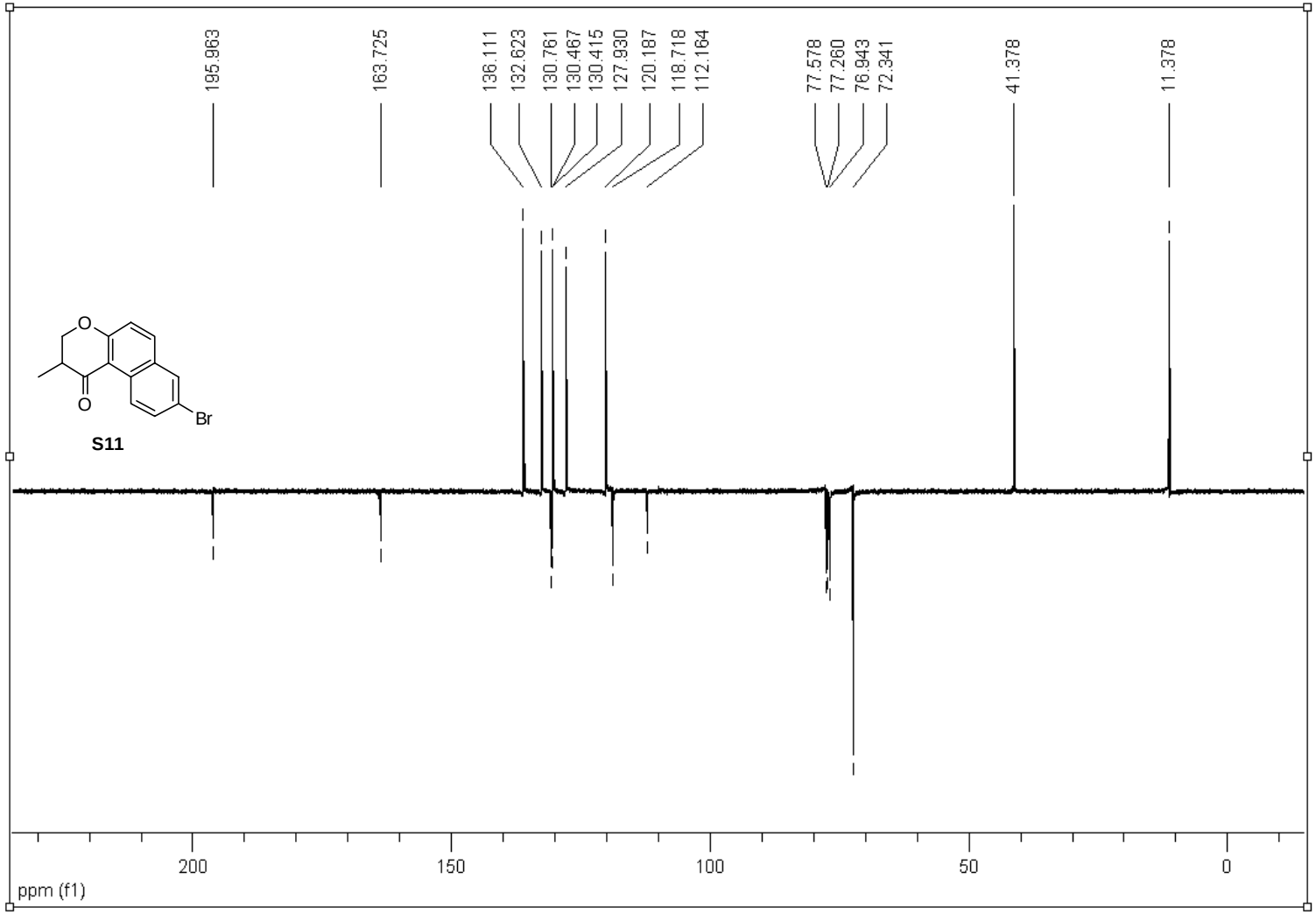
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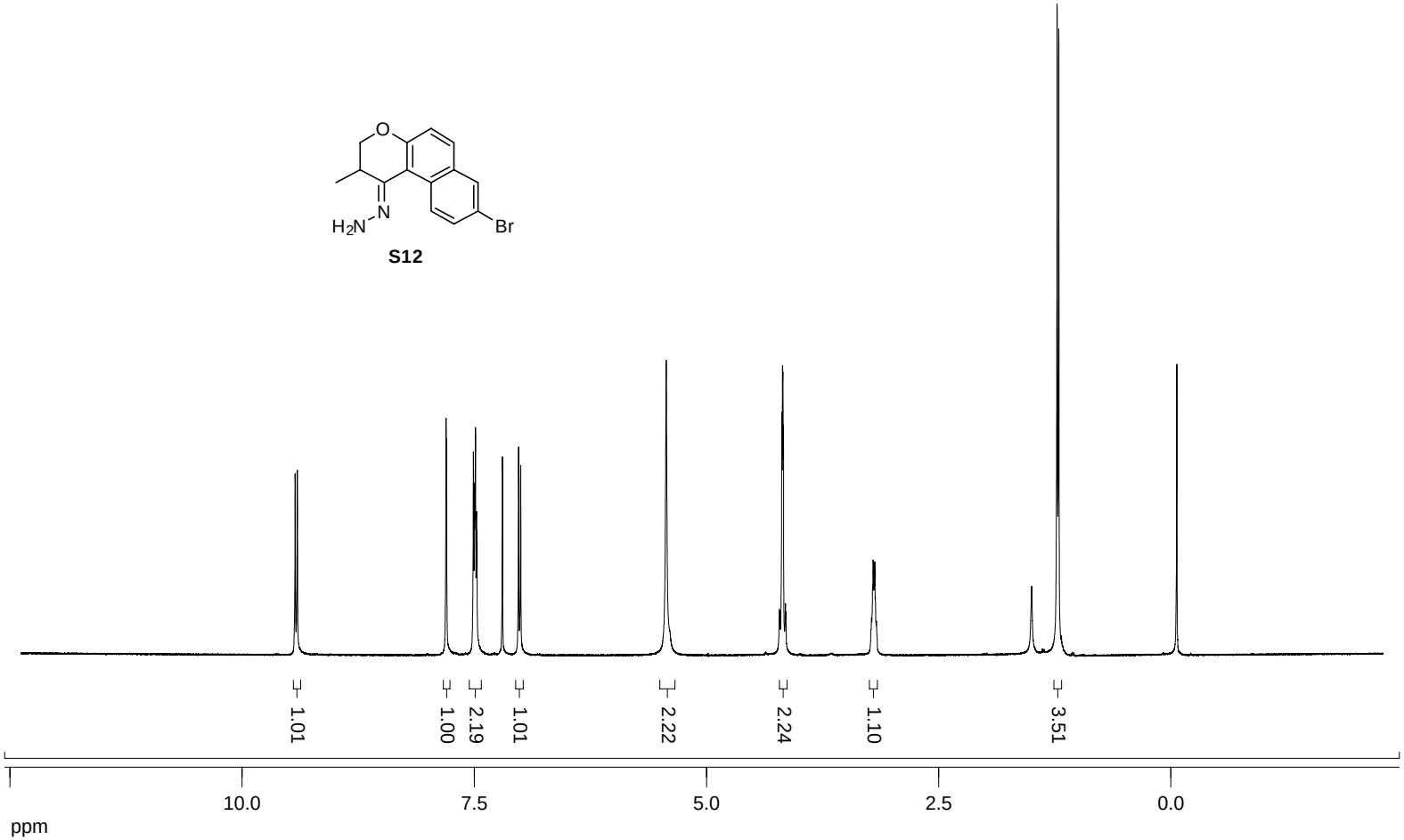
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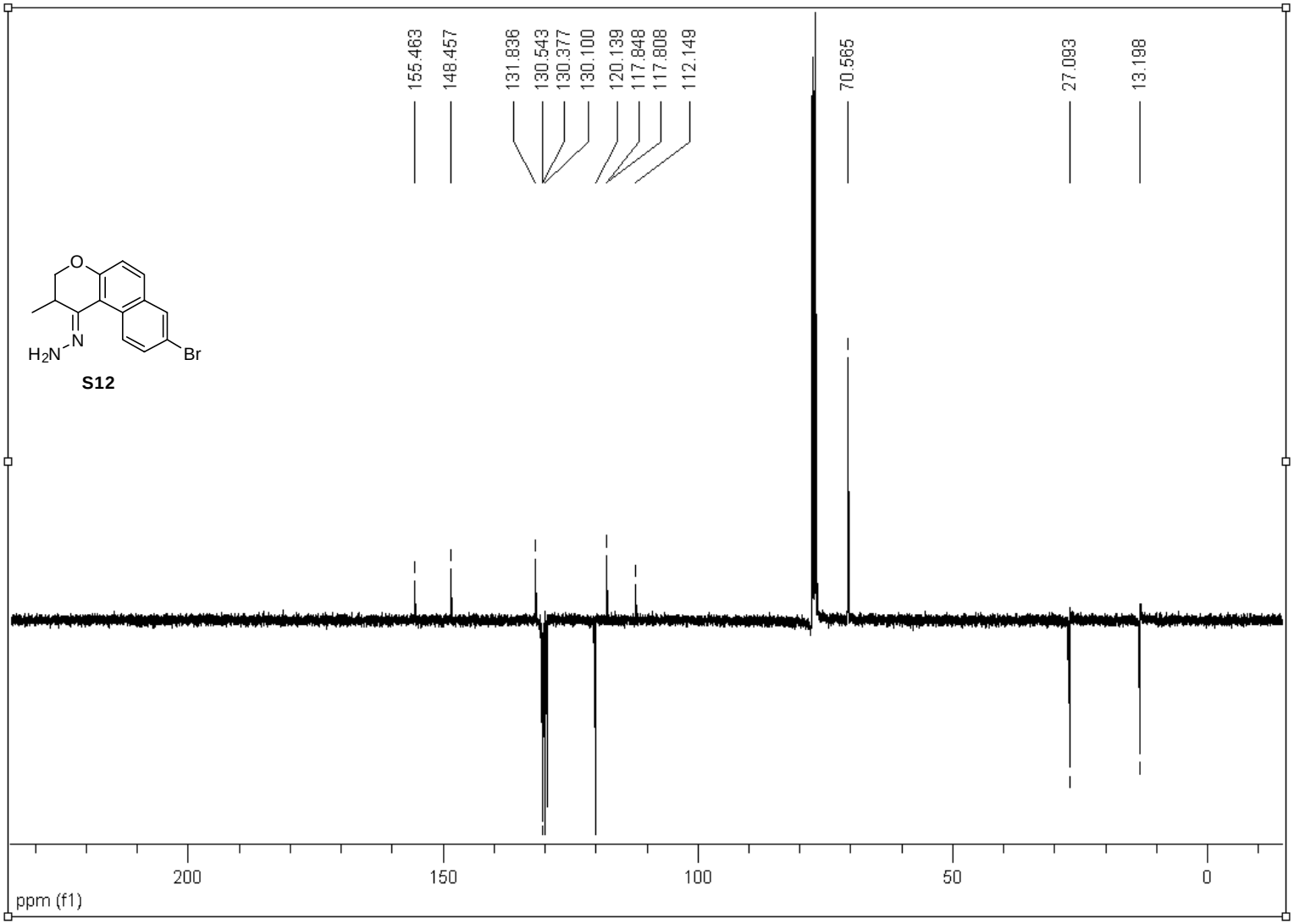
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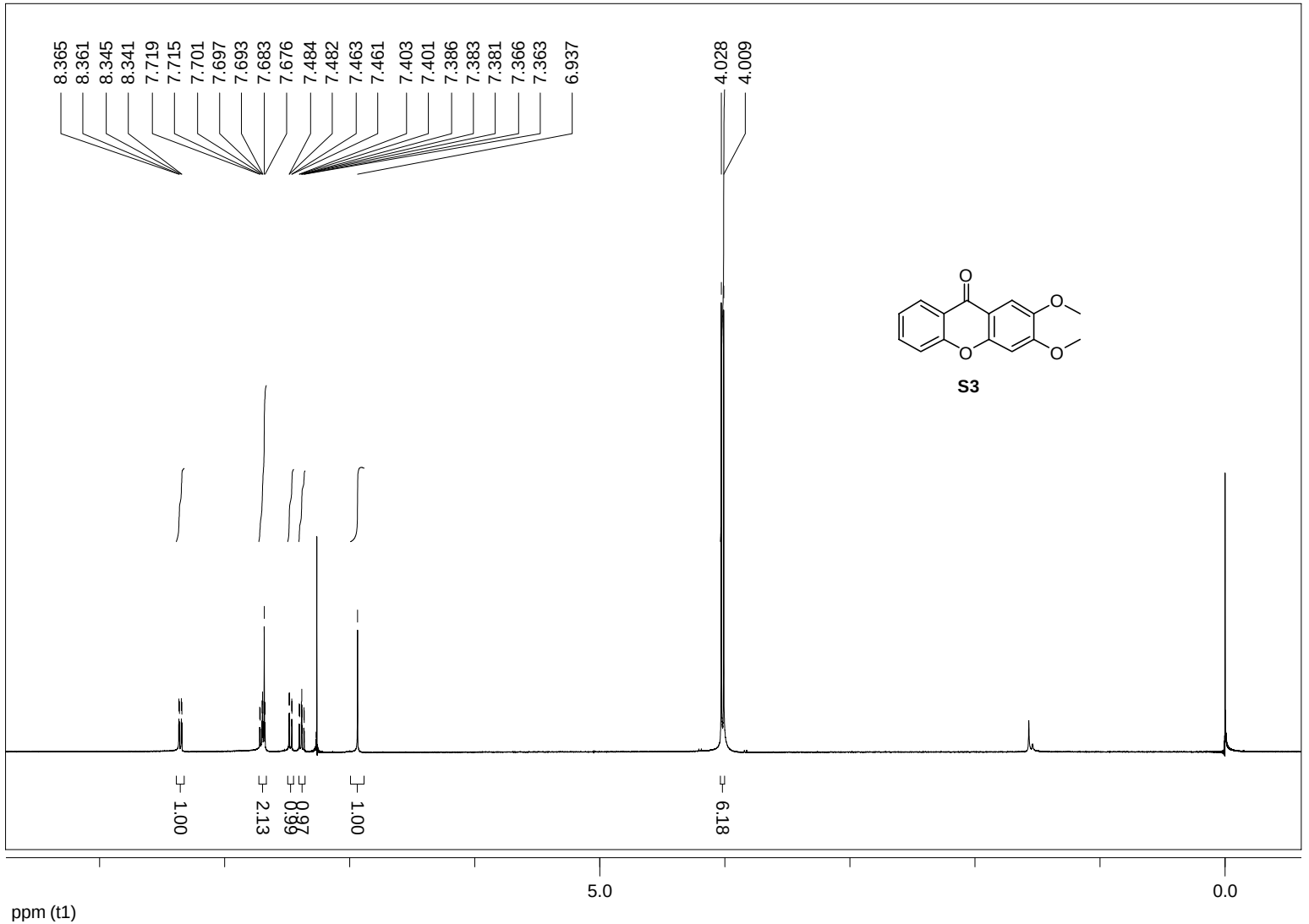
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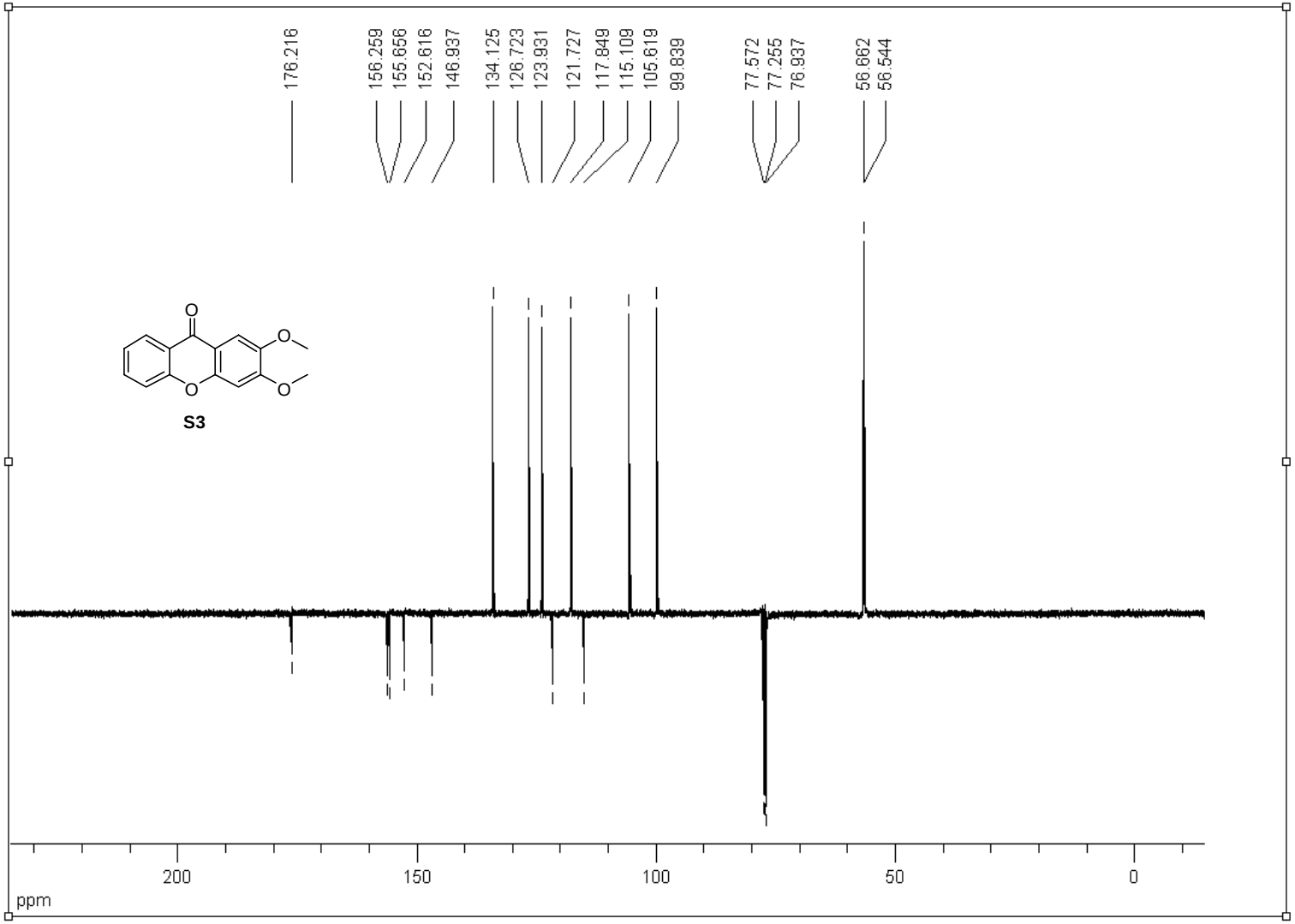
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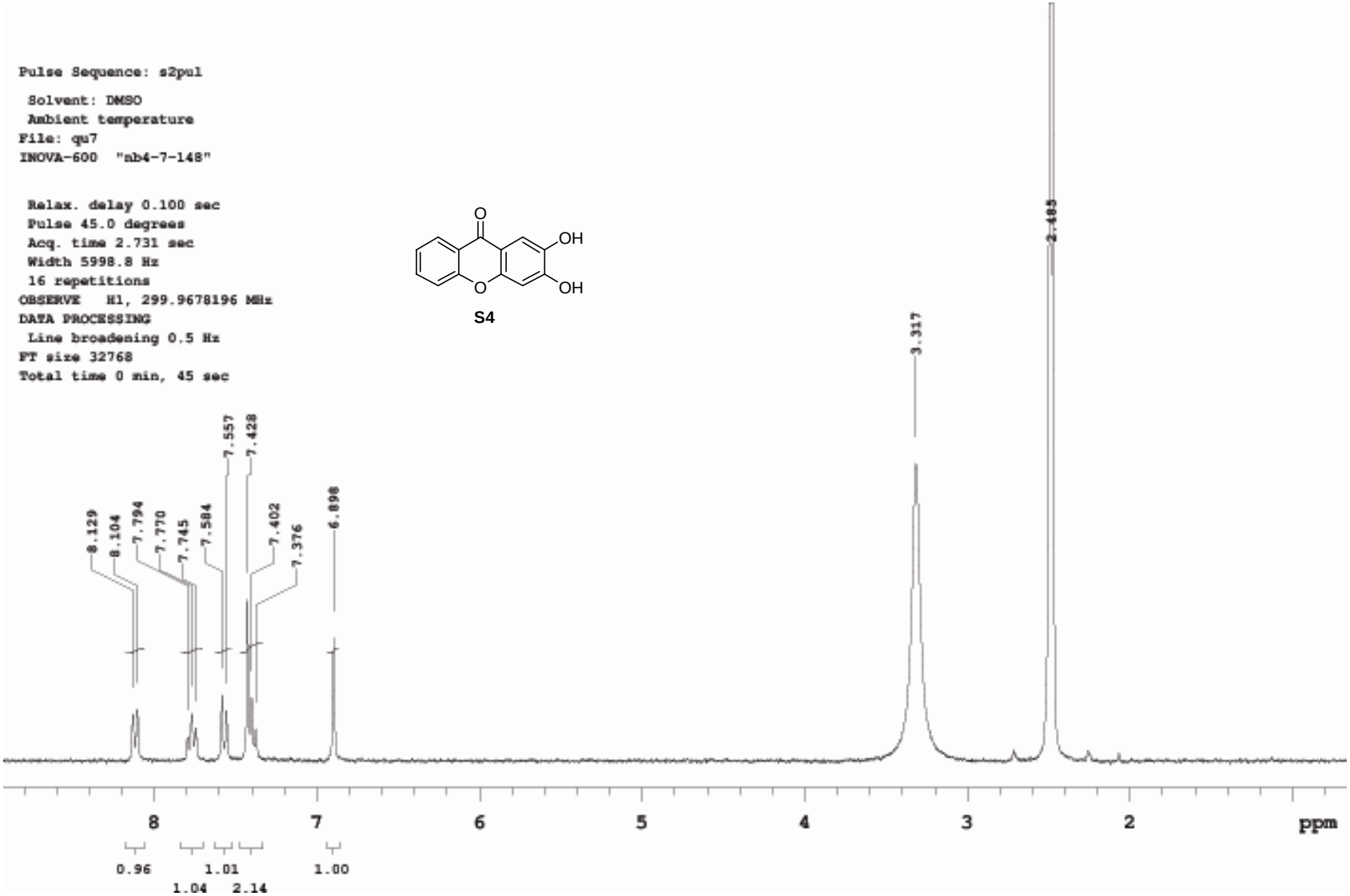
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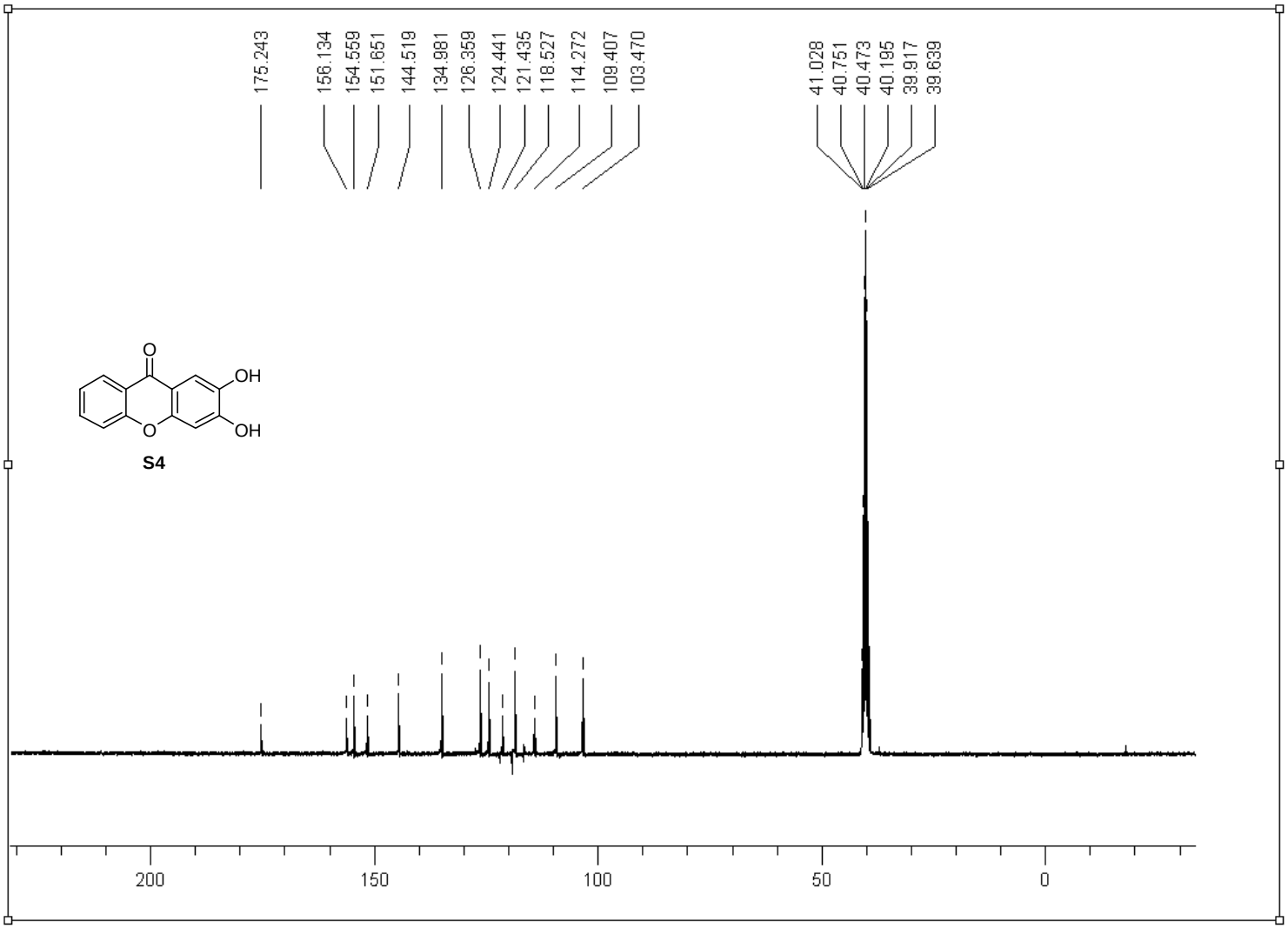
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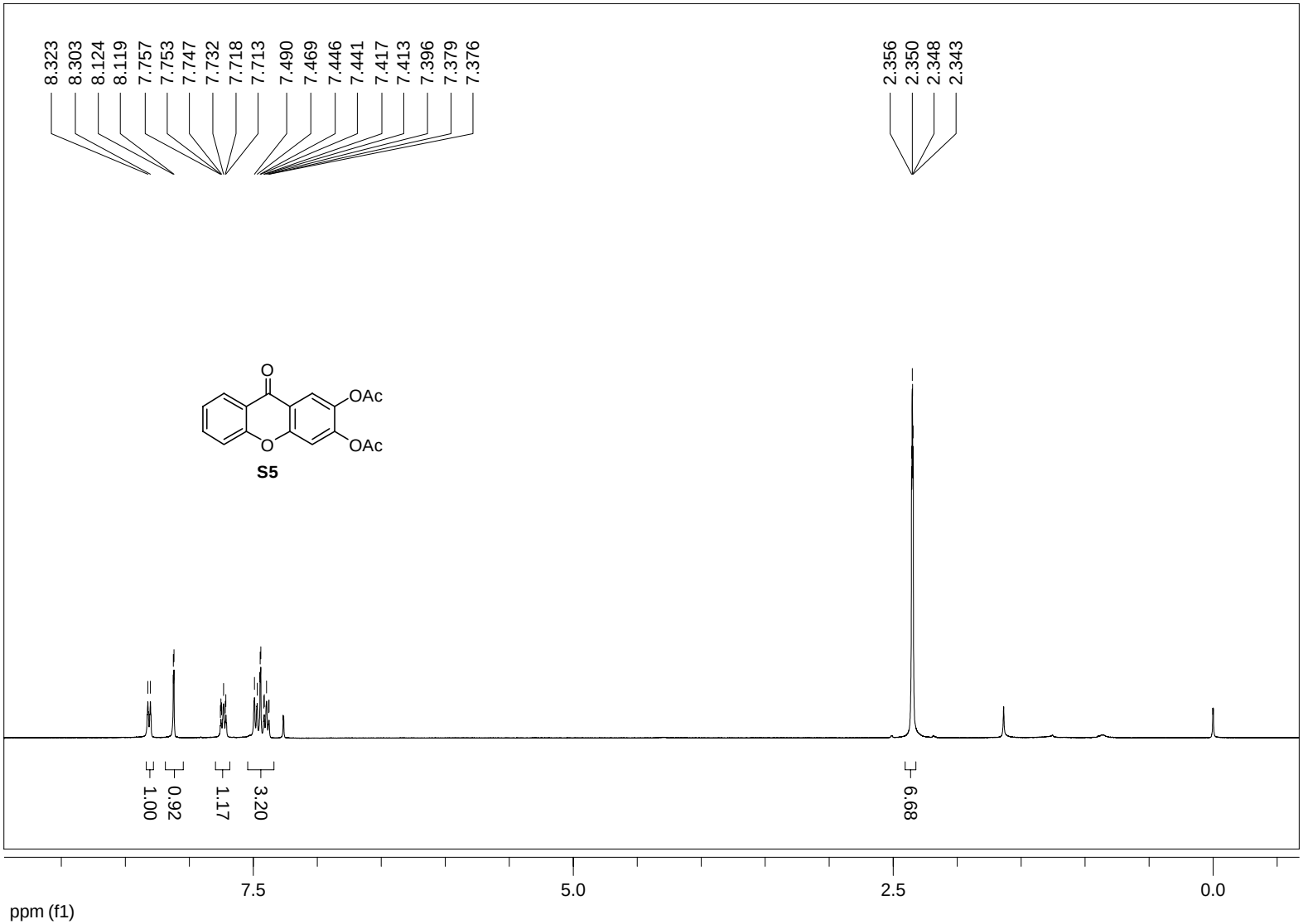
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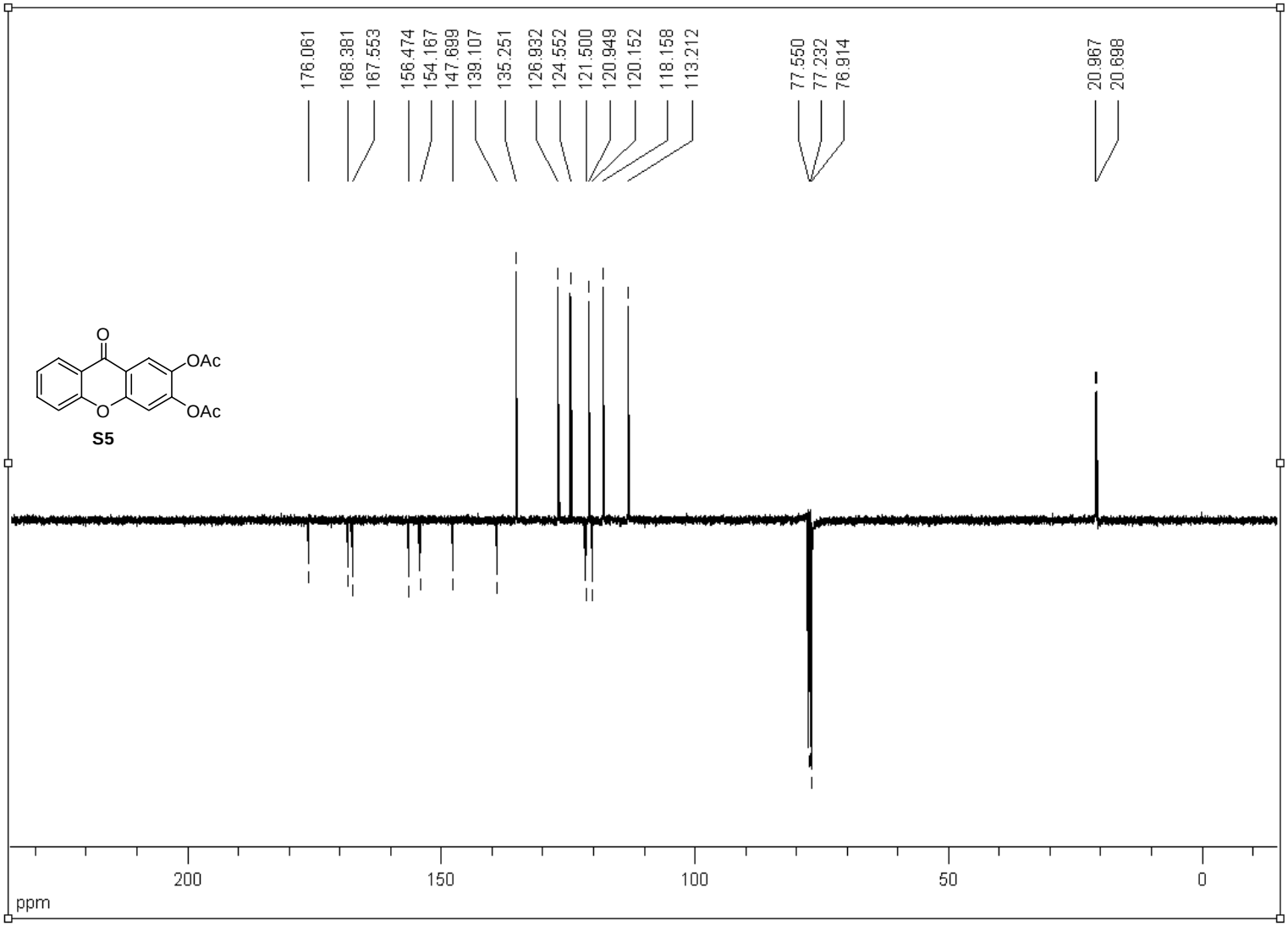
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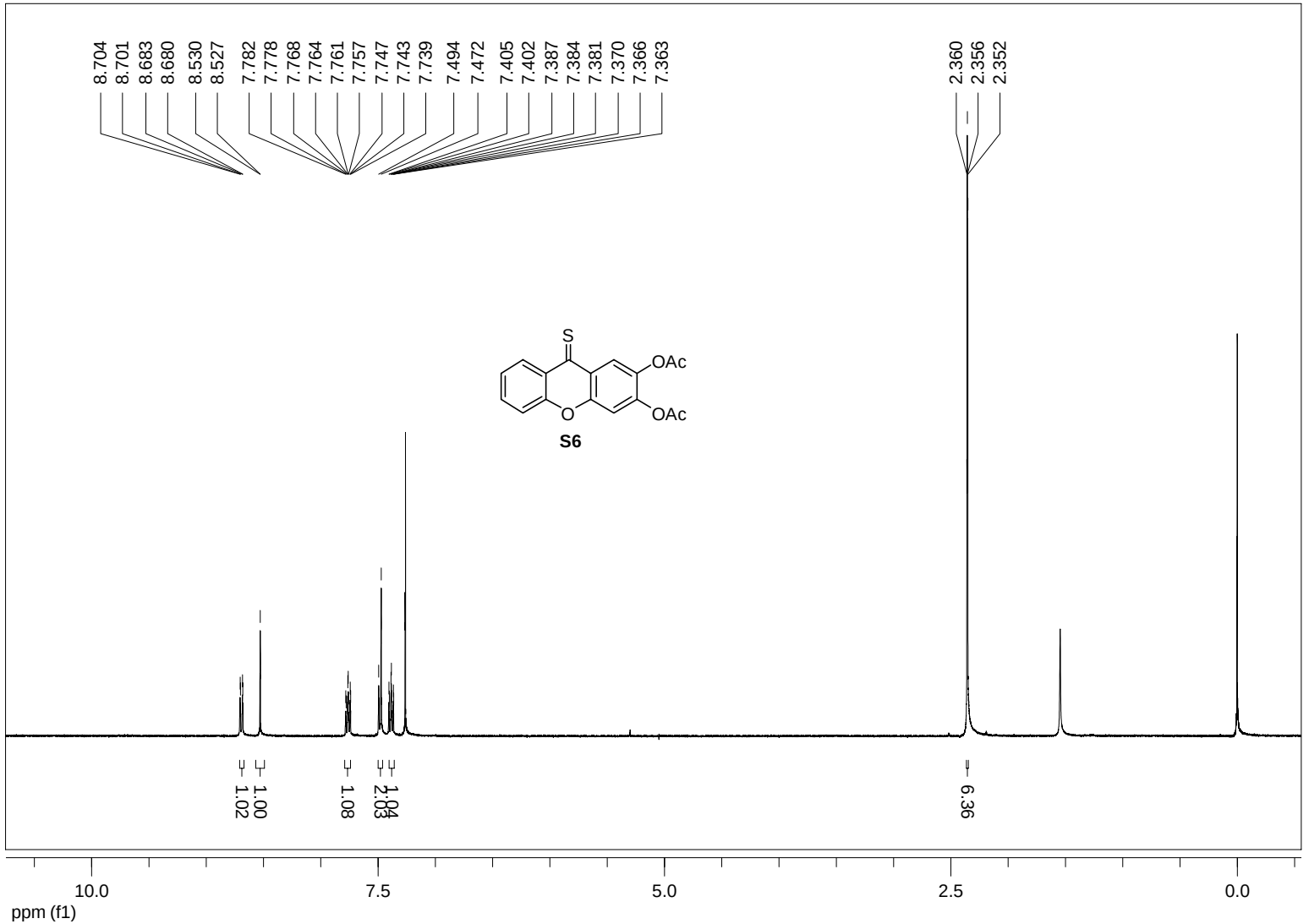
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OAc
O
S6
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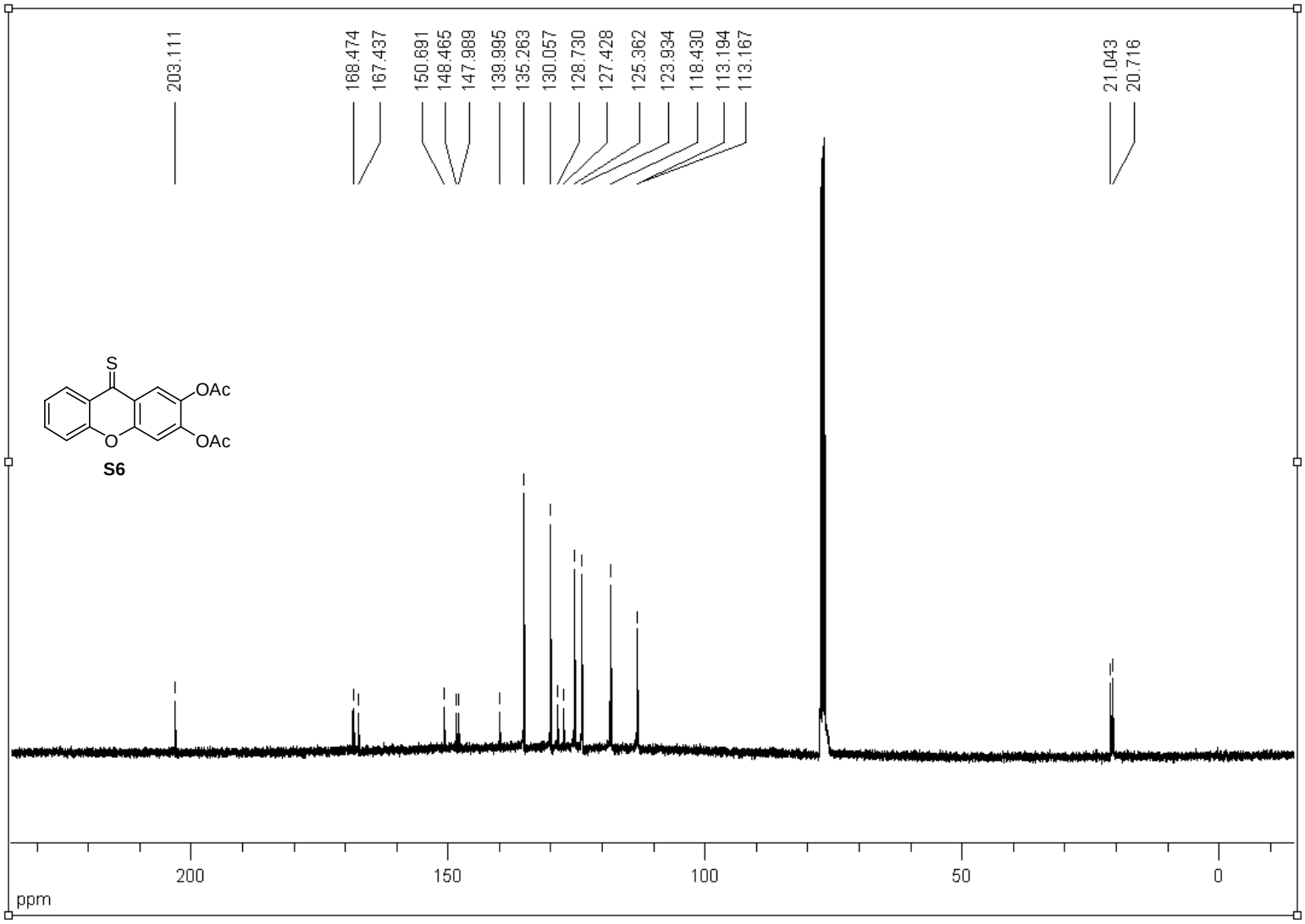
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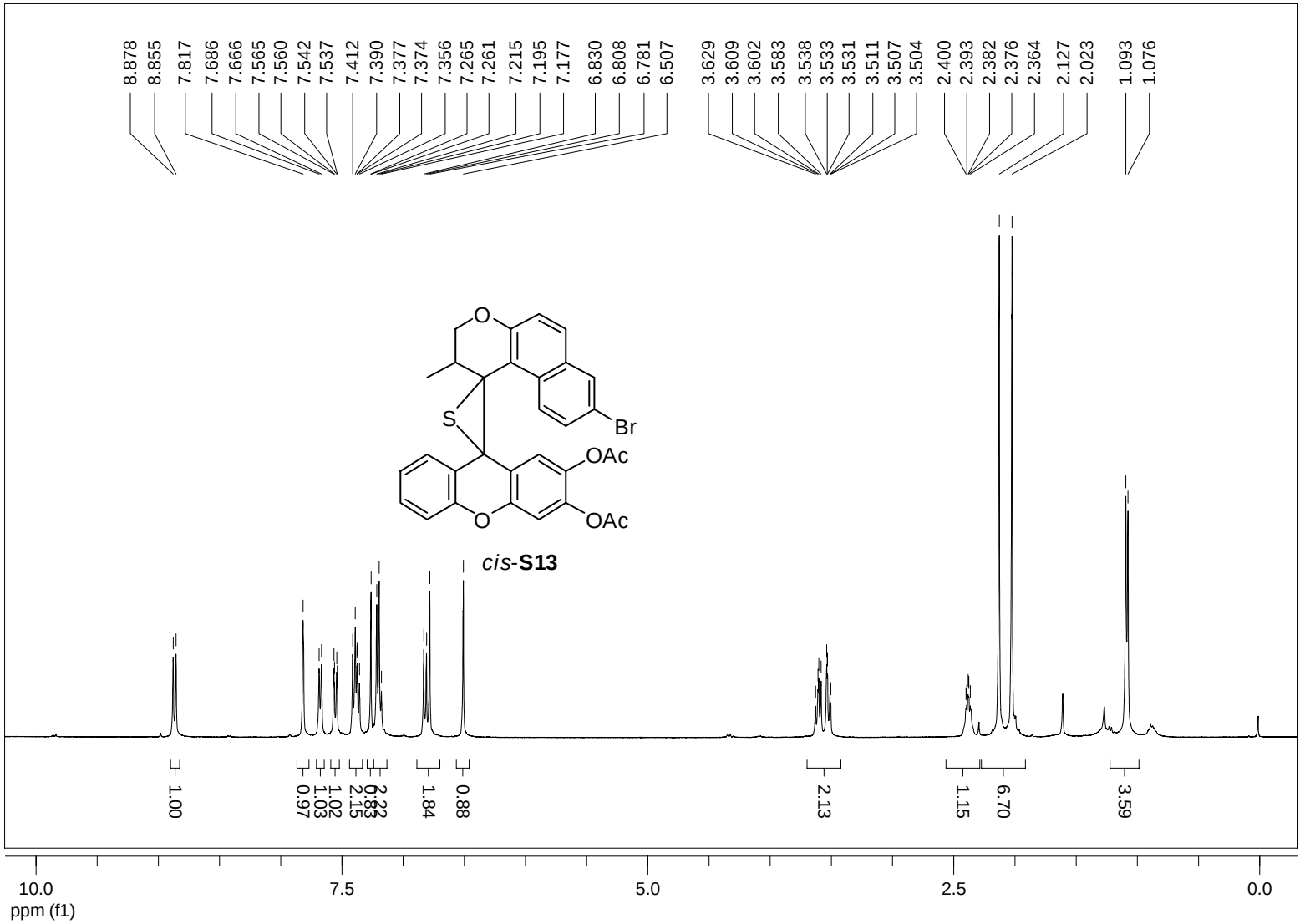
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S
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OAc
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cis-S13
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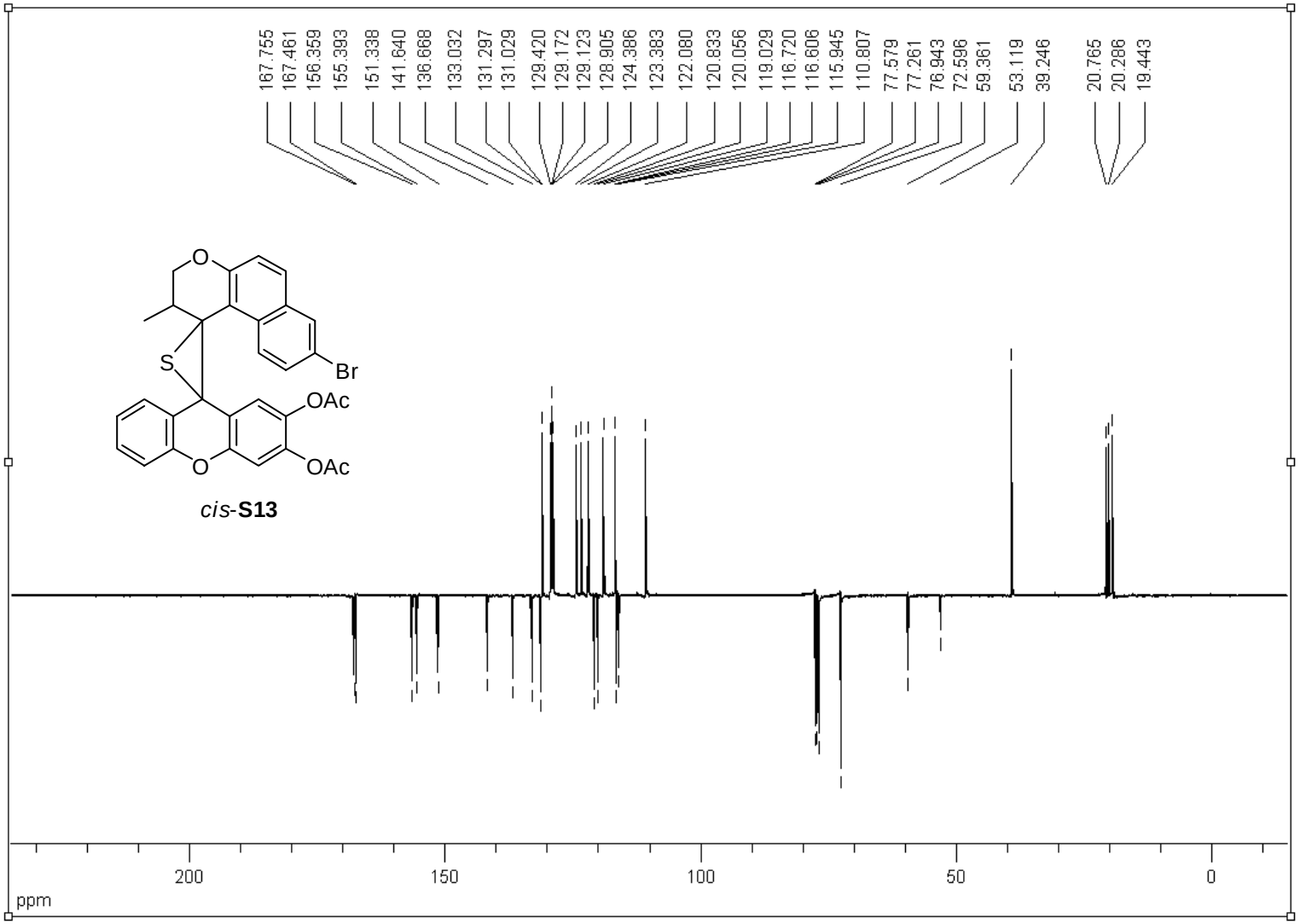
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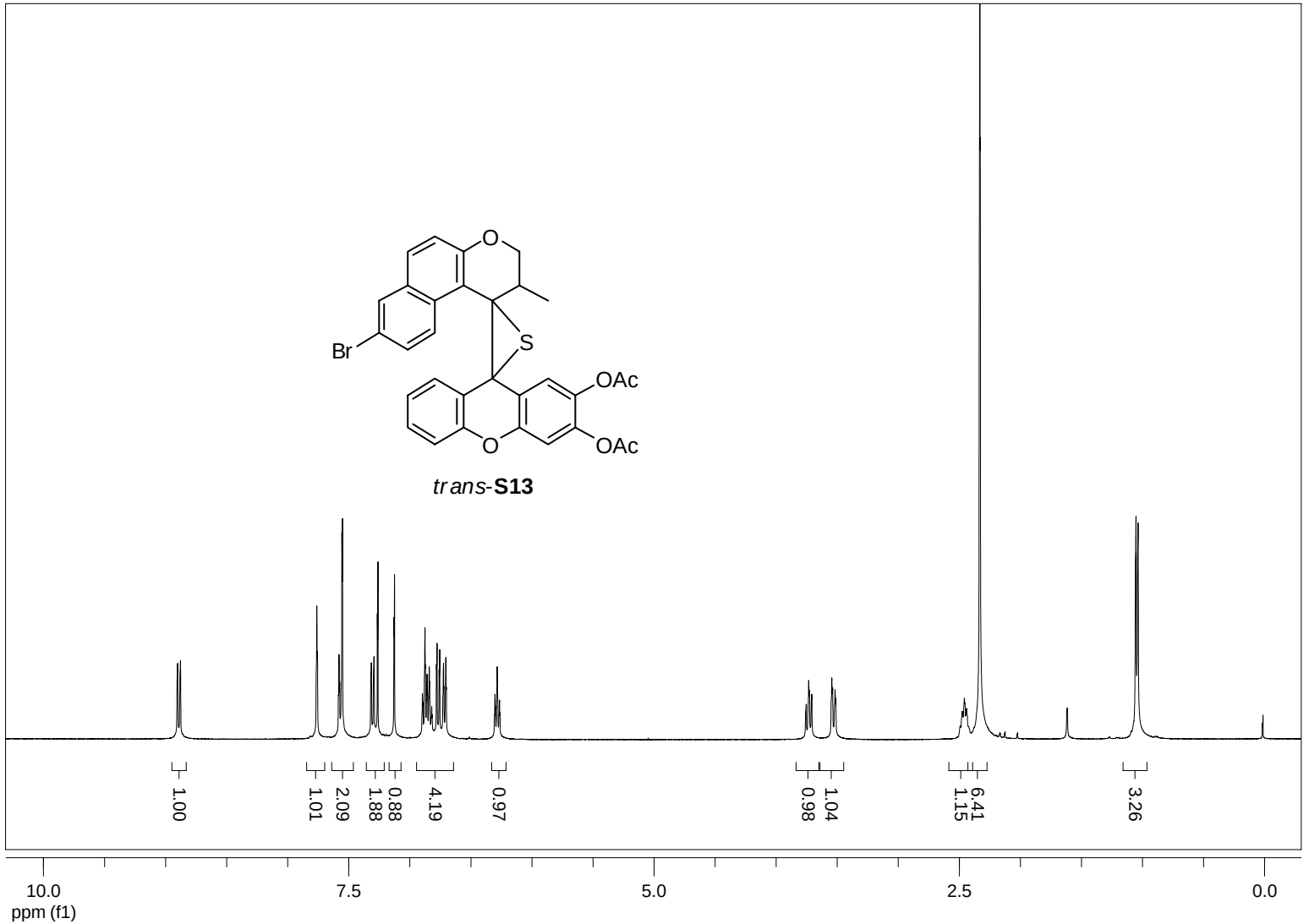
cis-**S13**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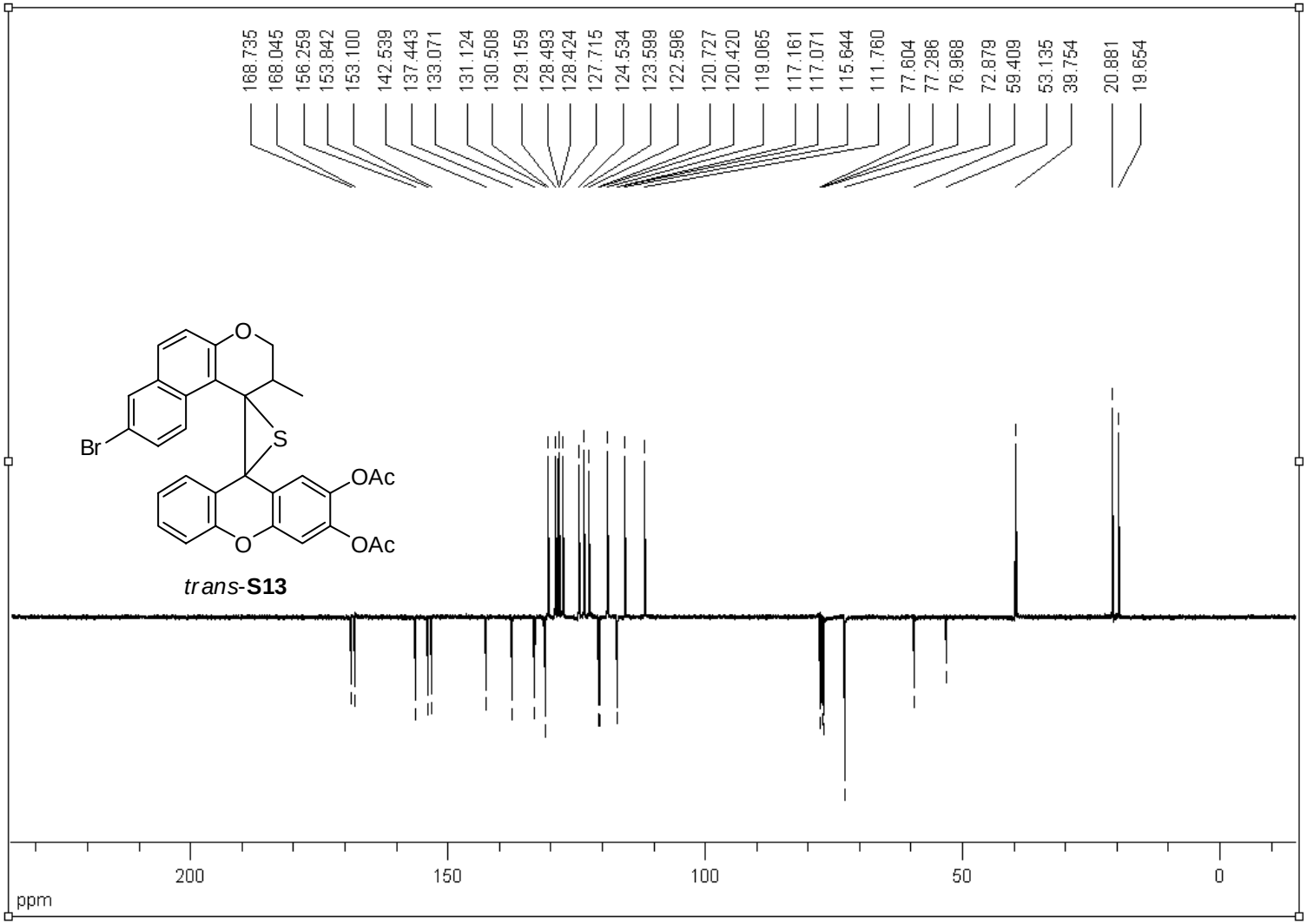
ppm (f1)

trans-**S13**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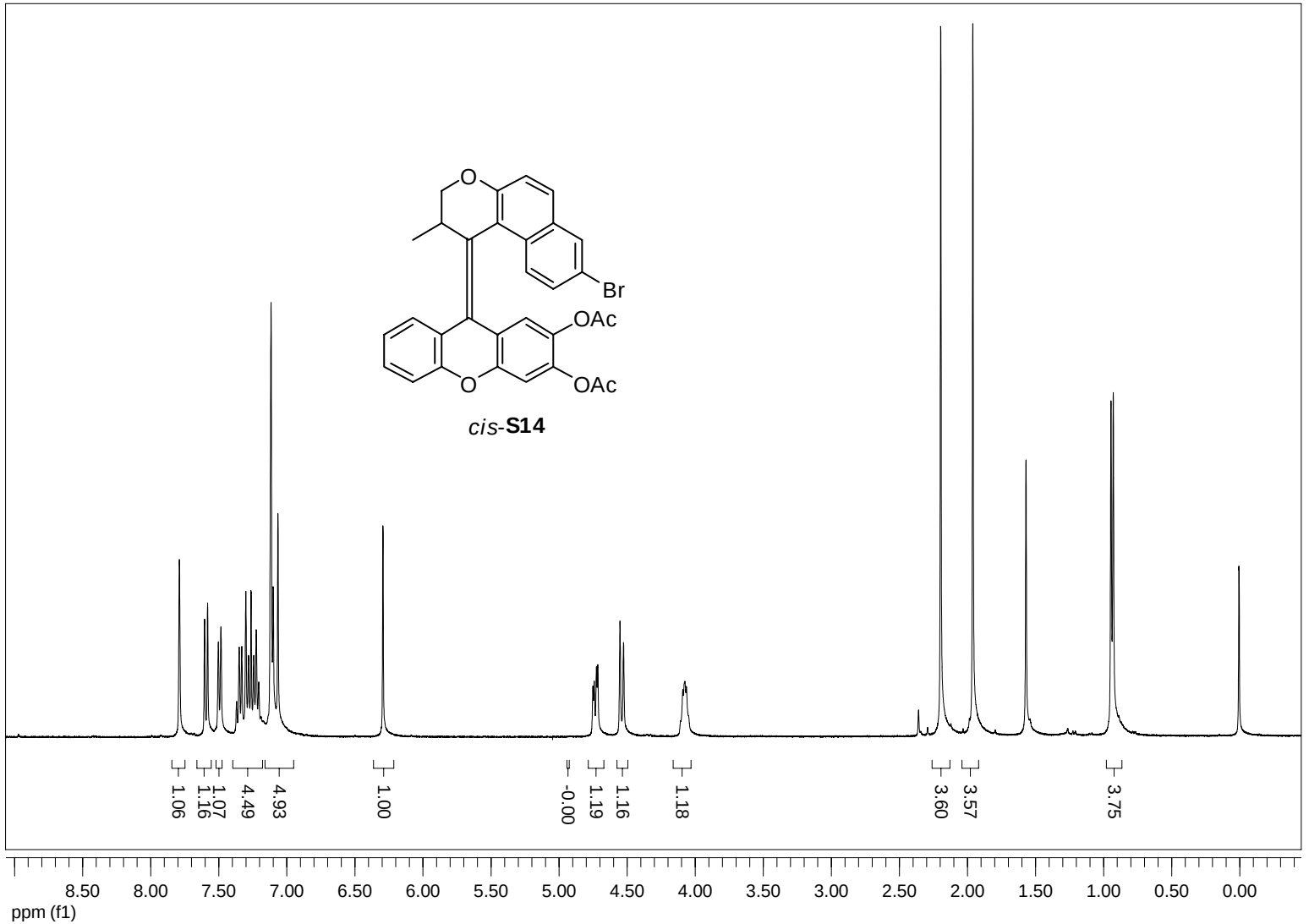
ppm

trans-**S13**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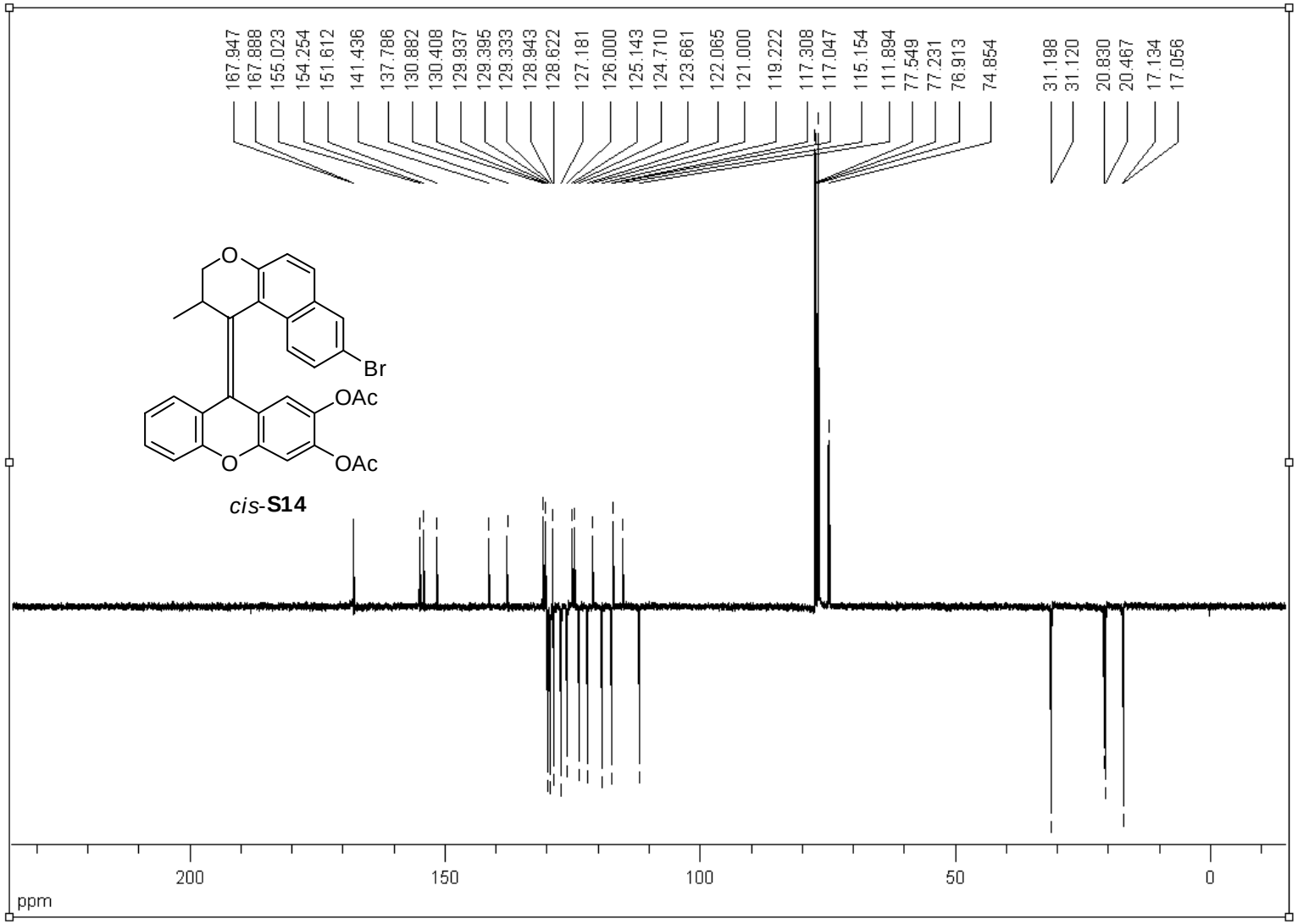
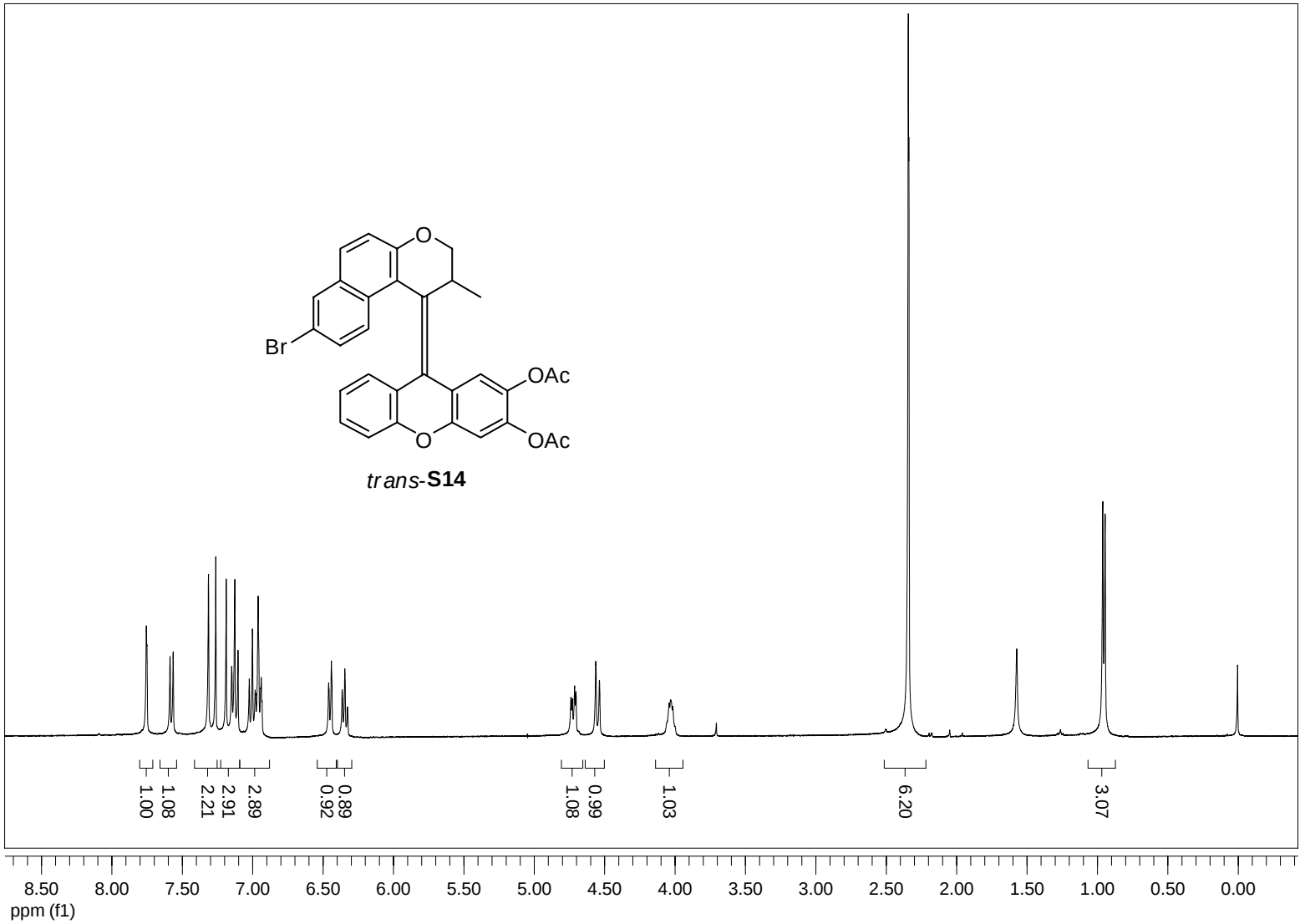
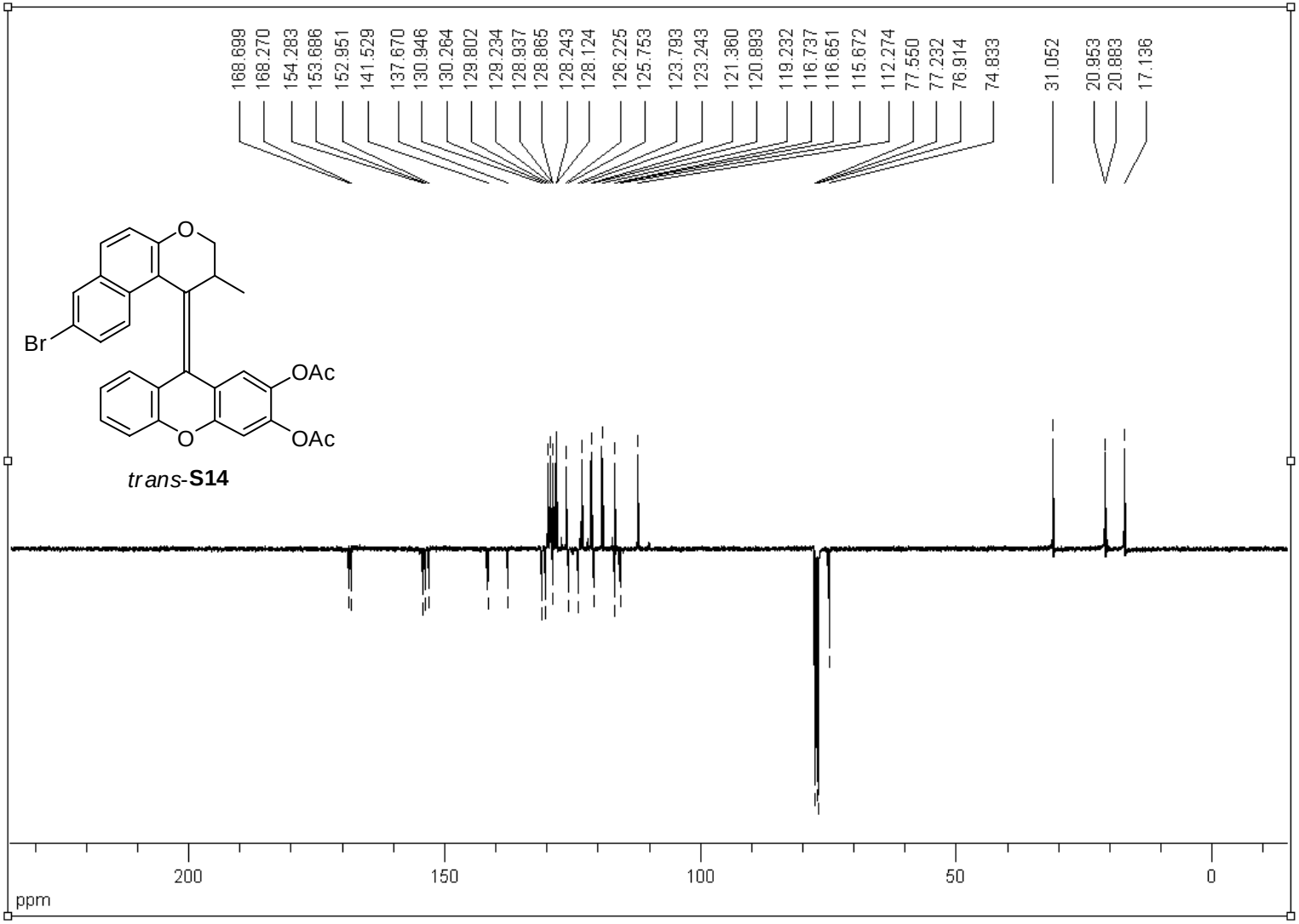
0.00
ppm (f1)


167.947
167.888
155.023
154.254
151.612
141.436
137.786
130.882
130.408
129.937
129.385
129.333
128.943
128.622
127.181
126.000
125.143
124.710
123.661
122.065
121.000
119.222
117.308
117.047
115.154
111.894
77.549
77.231
76.913
74.854
31.198
31.120
20.830
20.467
17.134
17.056
O
Br
OAc
OAc
O
200
150
100
50
0
ppm

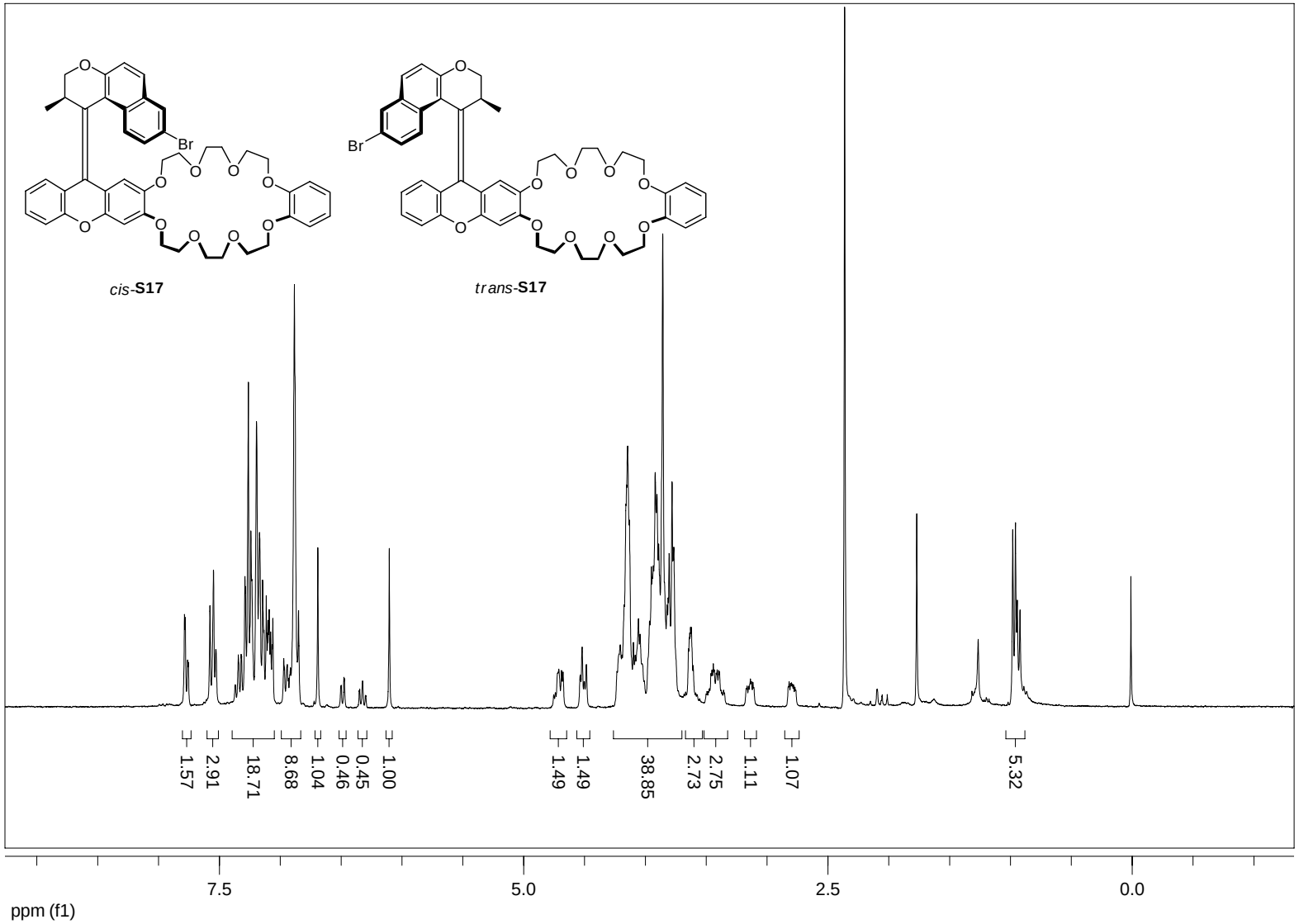
cis-**S14**

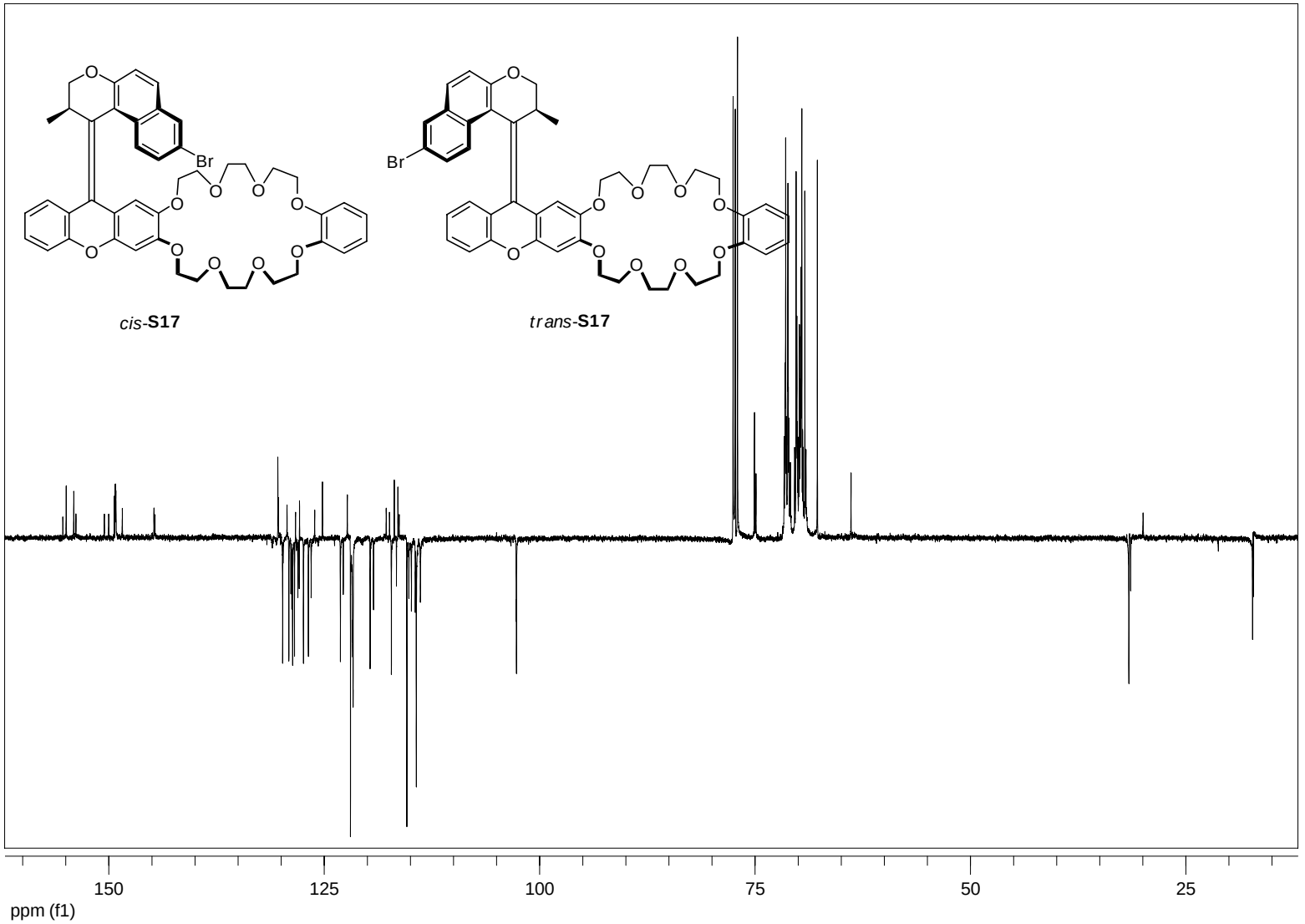

O
Br
OAc
OAc
O
1.00
1.08
2.21
2.91
2.89
0.92
0.89
1.08
0.99
1.03
6.20
3.07
8.50
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

trans-**S14**


168.699
168.270
154.283
153.686
152.951
141.529
137.670
130.946
130.264
129.802
129.234
128.937
128.865
128.243
128.124
126.225
125.753
123.793
123.243
121.360
120.893
119.232
116.737
116.651
115.672
112.274
77.550
77.232
76.914
74.833
31.052
20.953
20.883
17.136
O
Br
OAc
OAc
O
200
150
100
50
0
ppm

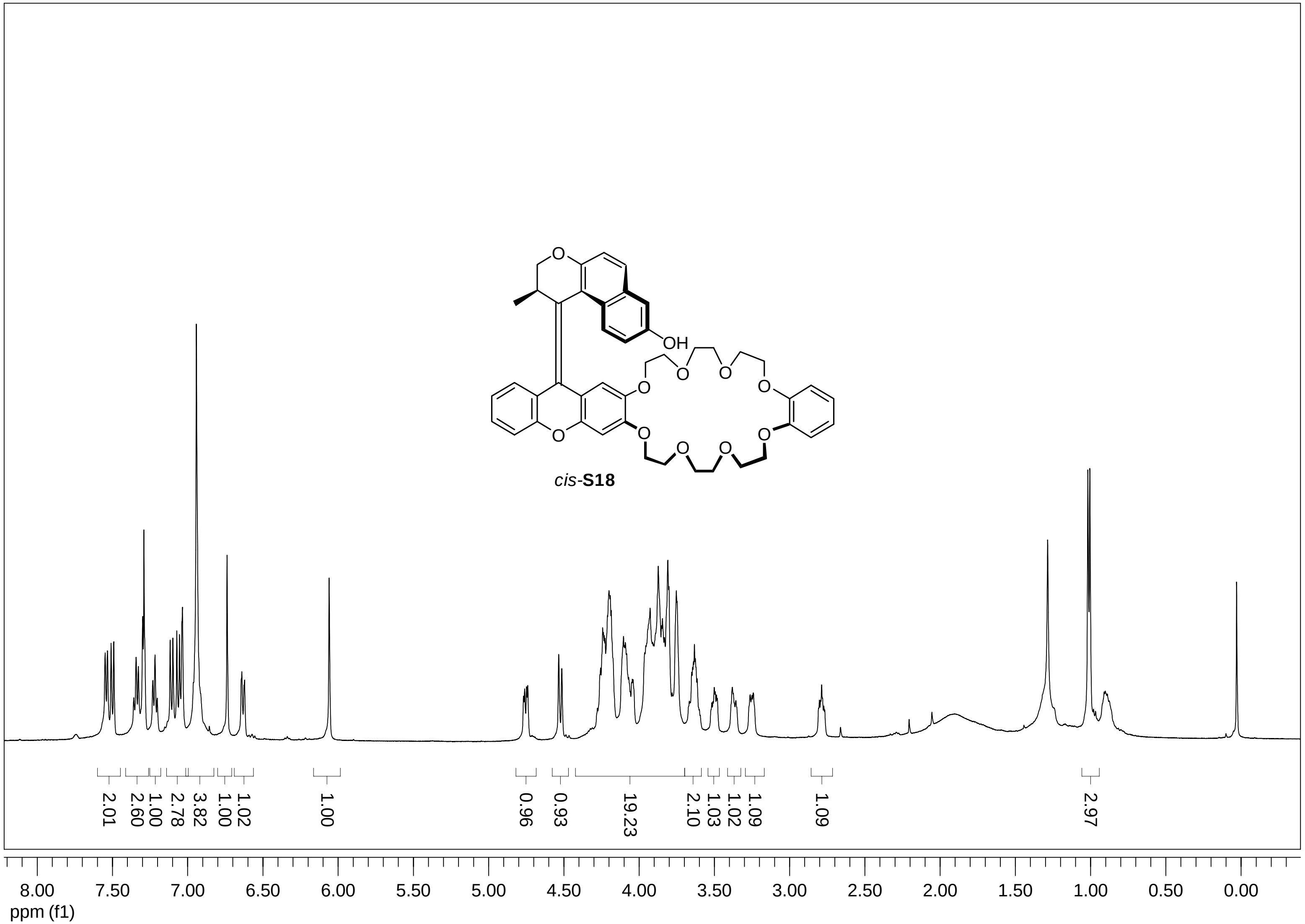
trans-**S14**

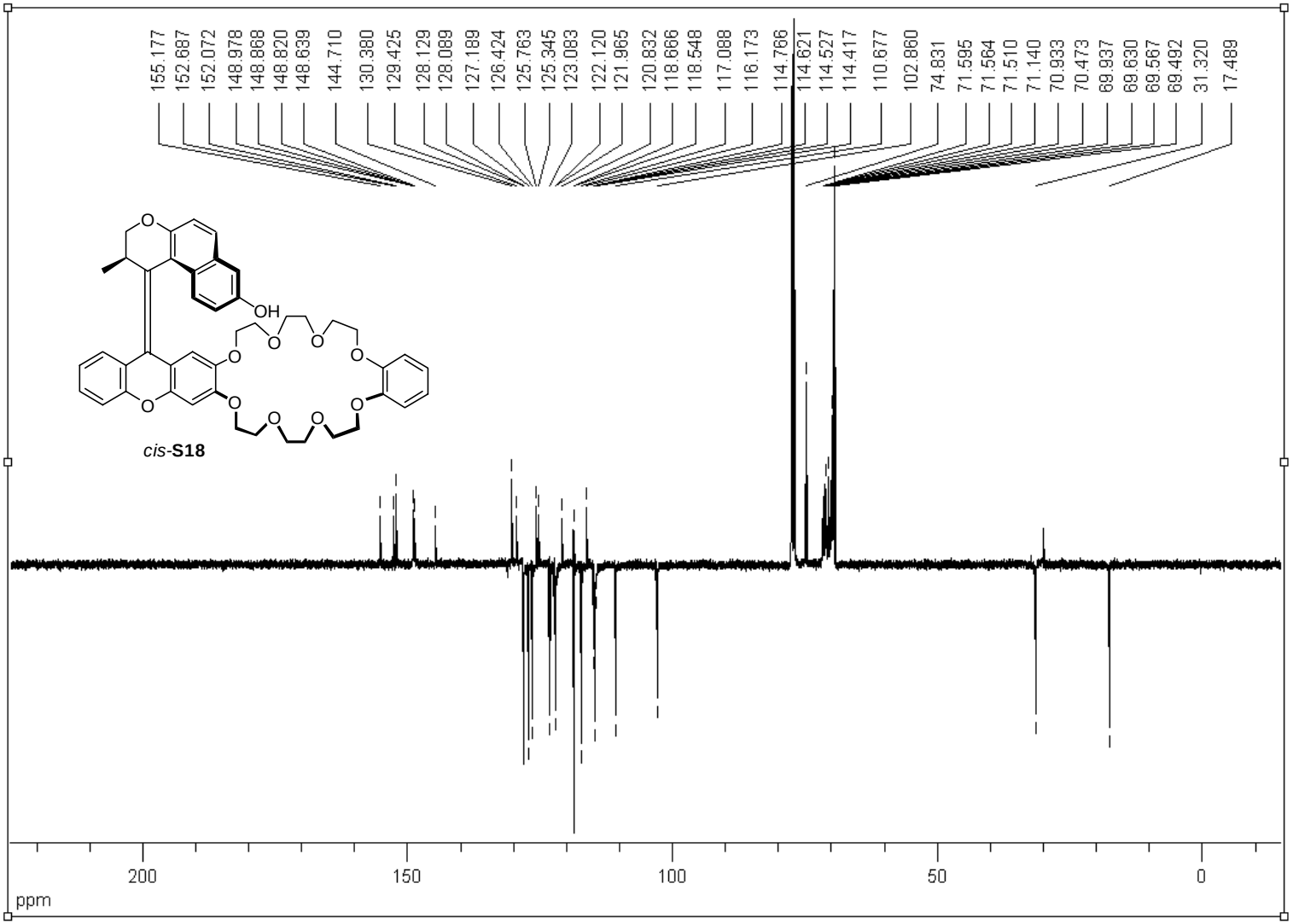

Br
Br
cis-S17
trans-S17
1.57
2.91
18.71
8.68
1.04
0.46
0.45
1.00
1.49
1.49
38.85
2.73
2.75
1.11
1.07
5.32
7.5
5.0
2.5
0.0
ppm (f1)



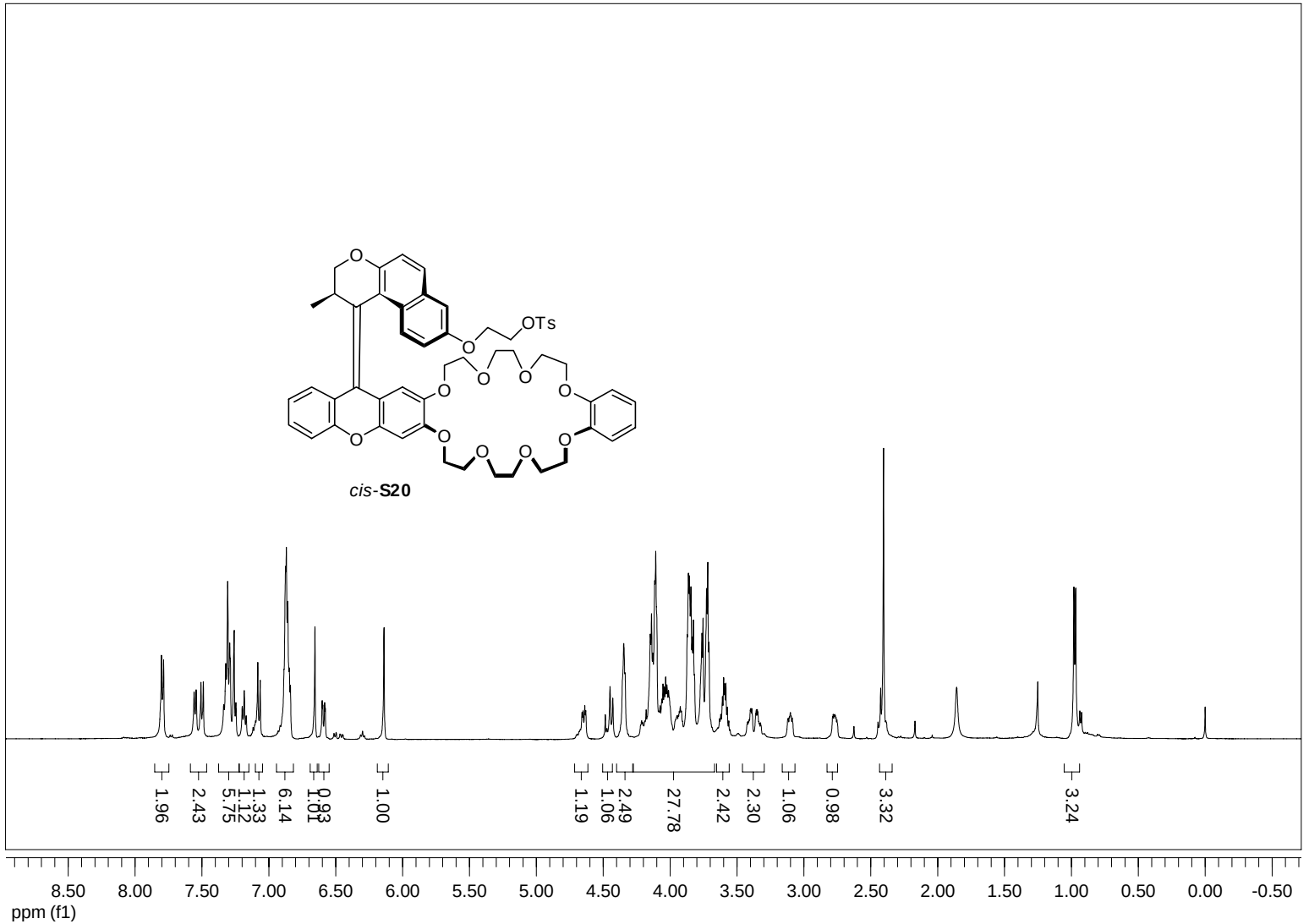
cis-**S17**

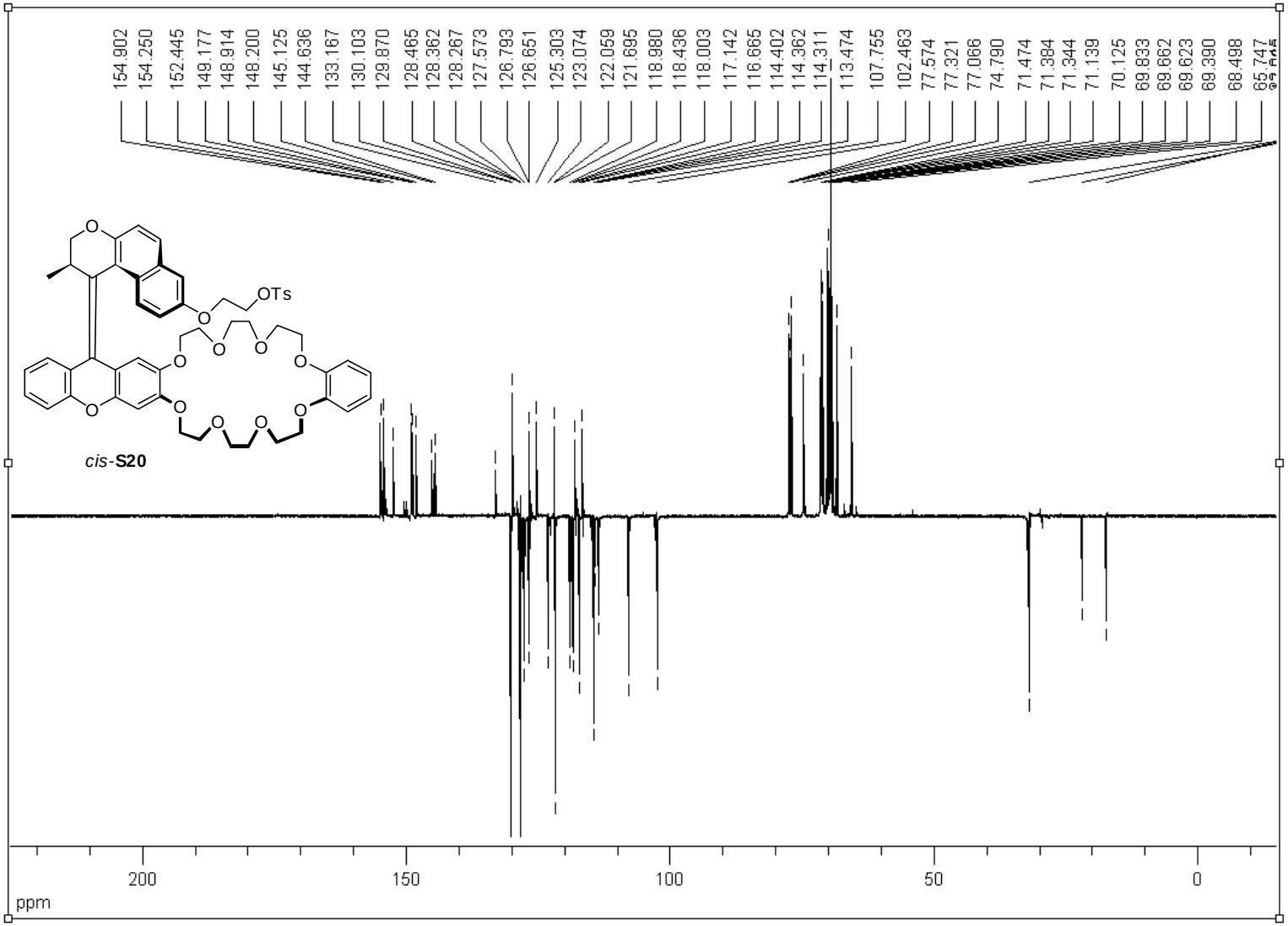
trans-**S17**

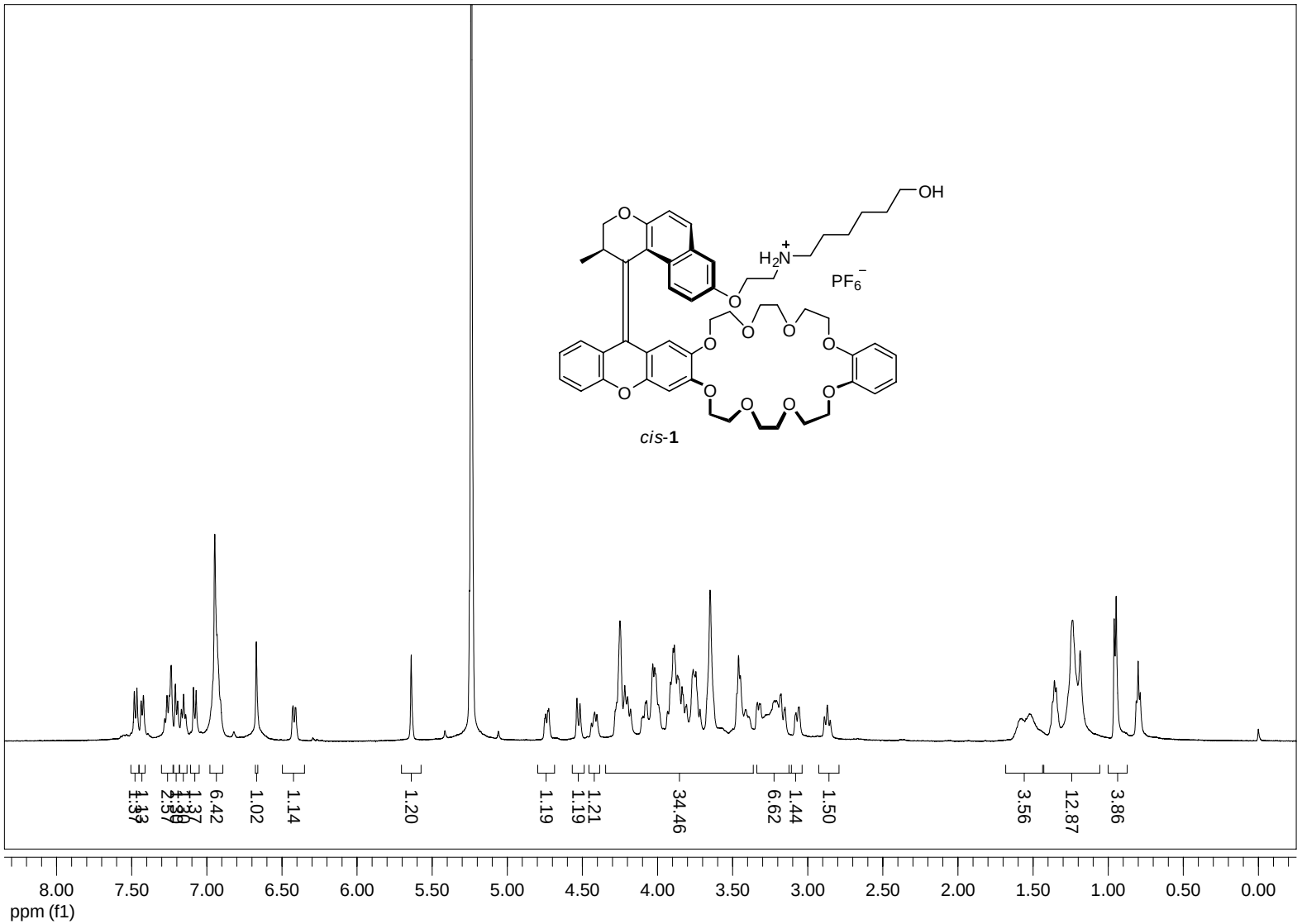

OH
O
cis-**S18**
2.01
2.60
1.00
2.78
3.82
1.00
1.02
1.00
0.96
0.93
19.23
2.10
1.03
1.02
1.09
1.09
2.97
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)

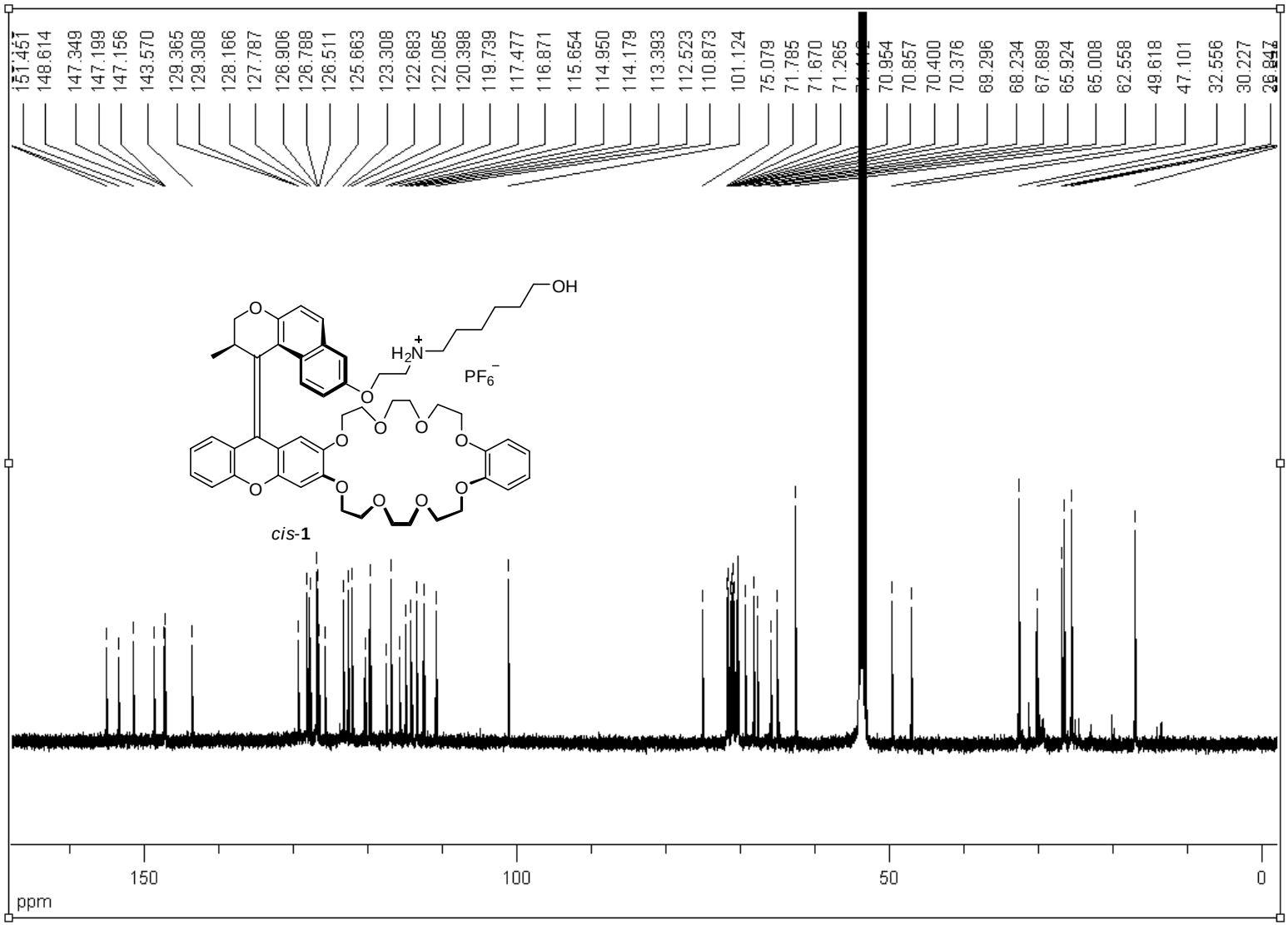

155.177
152.687
152.072
148.978
148.868
148.820
148.639
144.710
130.380
129.425
128.129
128.089
127.189
126.424
125.763
125.345
123.083
122.120
121.965
120.832
118.666
118.548
117.088
116.173
114.766
114.621
114.527
114.417
110.677
102.860
74.831
71.585
71.564
71.510
71.140
70.933
70.473
69.937
69.630
69.567
69.492
31.320
17.489
OH
O
200
150
100
50
0
ppm

cis-**S18**


OTs
cis-S20
1.96
2.43
5.75
1.12
1.33
6.14
1.00
1.19
1.06
2.49
27.78
2.42
2.30
1.06
0.98
3.32
3.24
8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00 -0.50
ppm (f1)


154.902
154.250
152.445
149.177
148.914
148.200
145.125
144.636
133.167
130.103
129.870
128.465
128.362
128.267
127.573
126.793
126.651
125.303
123.074
122.059
121.695
118.980
118.436
118.003
117.142
116.665
114.402
114.362
114.311
113.474
107.755
102.463
77.574
77.321
77.066
74.790
71.474
71.384
71.344
71.139
70.125
69.833
69.662
69.623
69.390
68.498
65.747
OTs
cis-S20
200
150
100
50
0
ppm


OH
H2N
PF6−
O
cis-1
1.37
6.42
1.02
1.14
1.20
1.19
1.21
1.19
34.46
6.62
1.44
1.50
3.56
12.87
3.86
8.00
7.50
7.00
6.50
6.00
5.50
5.00
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
ppm (f1)


151.451
148.614
147.349
147.199
147.156
143.570
129.365
129.308
128.166
127.787
126.906
126.788
126.511
125.663
123.308
122.683
122.085
120.398
119.739
117.477
116.871
115.654
114.950
114.179
113.393
112.523
110.873
101.124
75.079
71.785
71.670
71.265
70.954
70.857
70.400
70.376
69.296
68.234
67.689
65.924
65.008
62.558
49.618
47.101
32.556
30.227
OH
H_2N^+
PF_6^-
O
cis-**1**
150
100
50
0
ppm